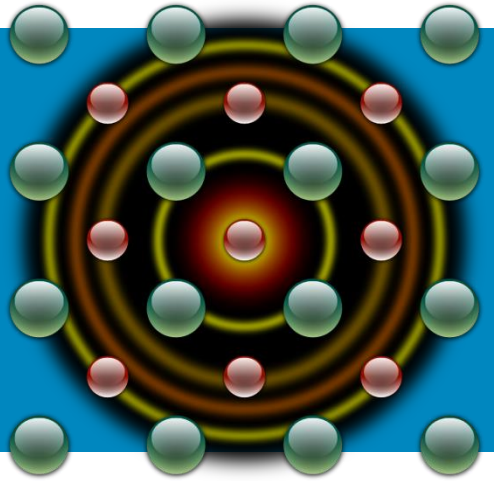
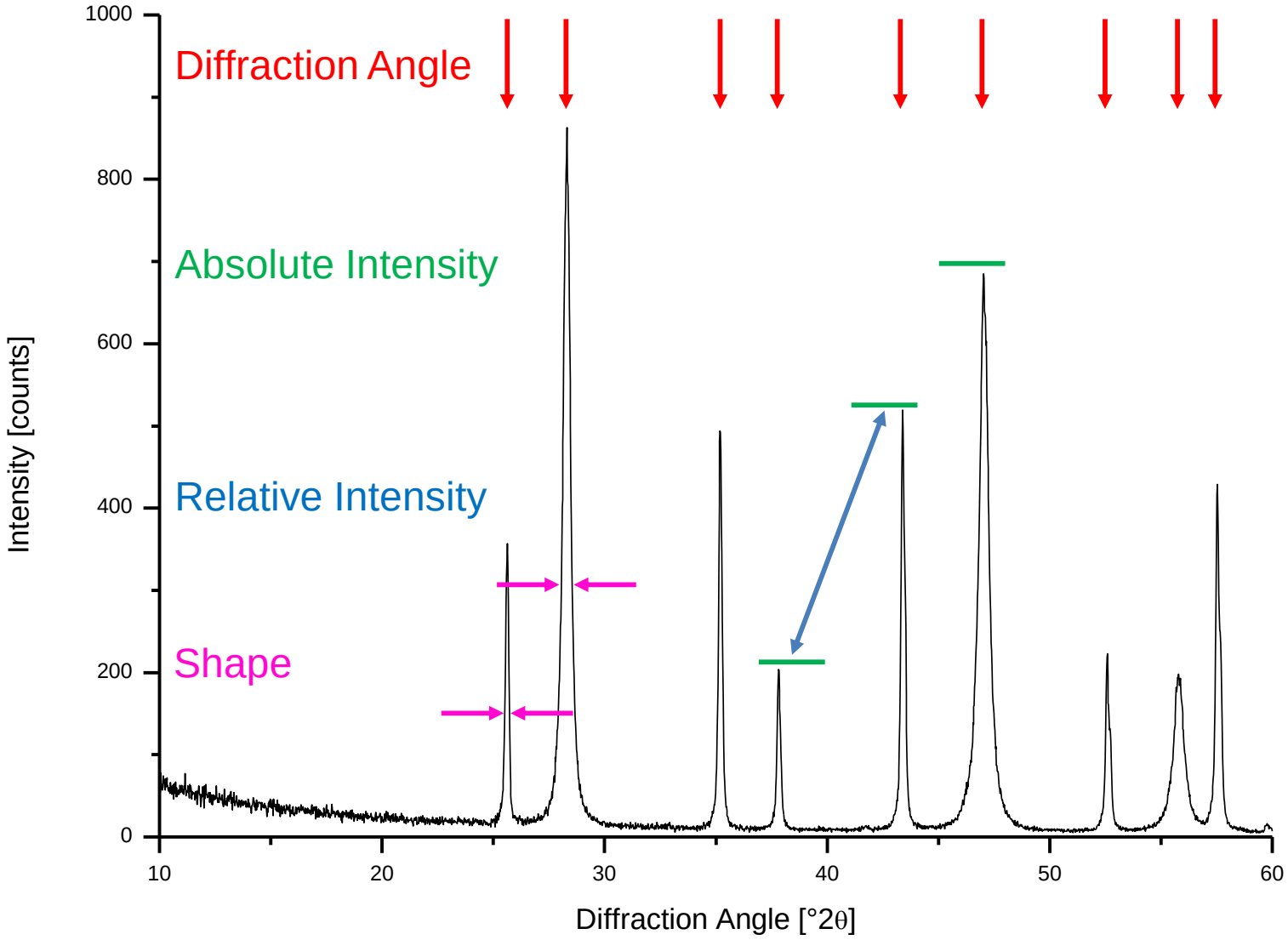
Lesson 1
Rietveld Refinement
and Profex / BGMN



Nicola Döbelin
RMS Foundation, Bettlach, Switzerland

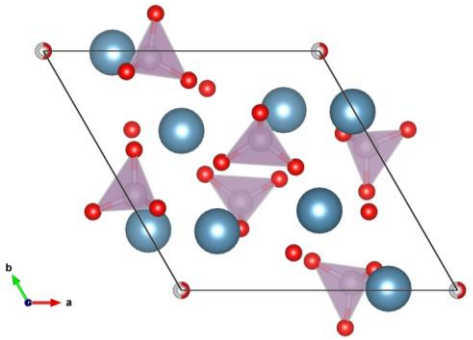
Diffraction Pattern



Diffraction Pattern

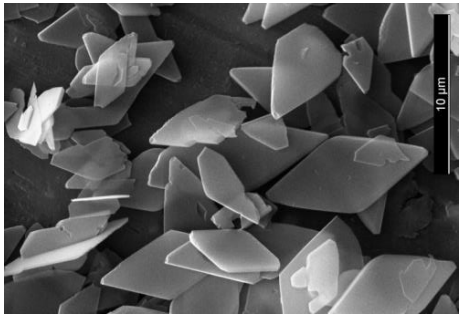
Diffraction Angle:
Phase Identification

Relative Intensity:
Crystal Structure Determination



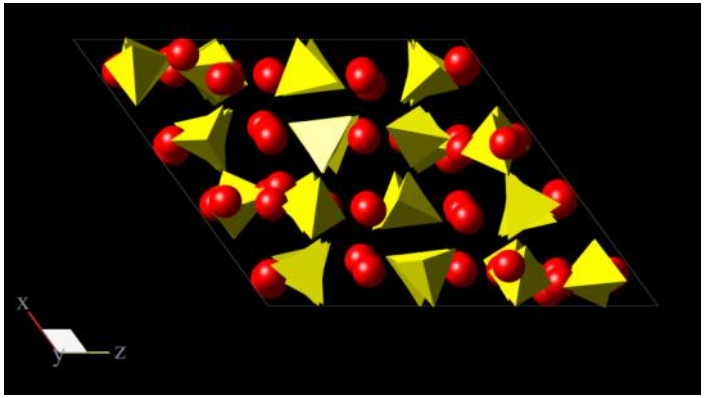
Absolute Intensity:
Phase Quantification

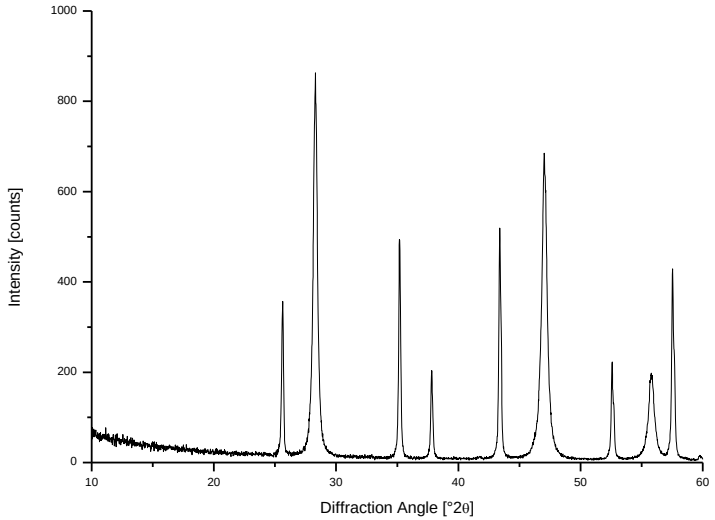
Shape:
Crystallite Size and Shape, Lattice Strain



Phase Identification

«Pattern Features» originate from crystallographic properties

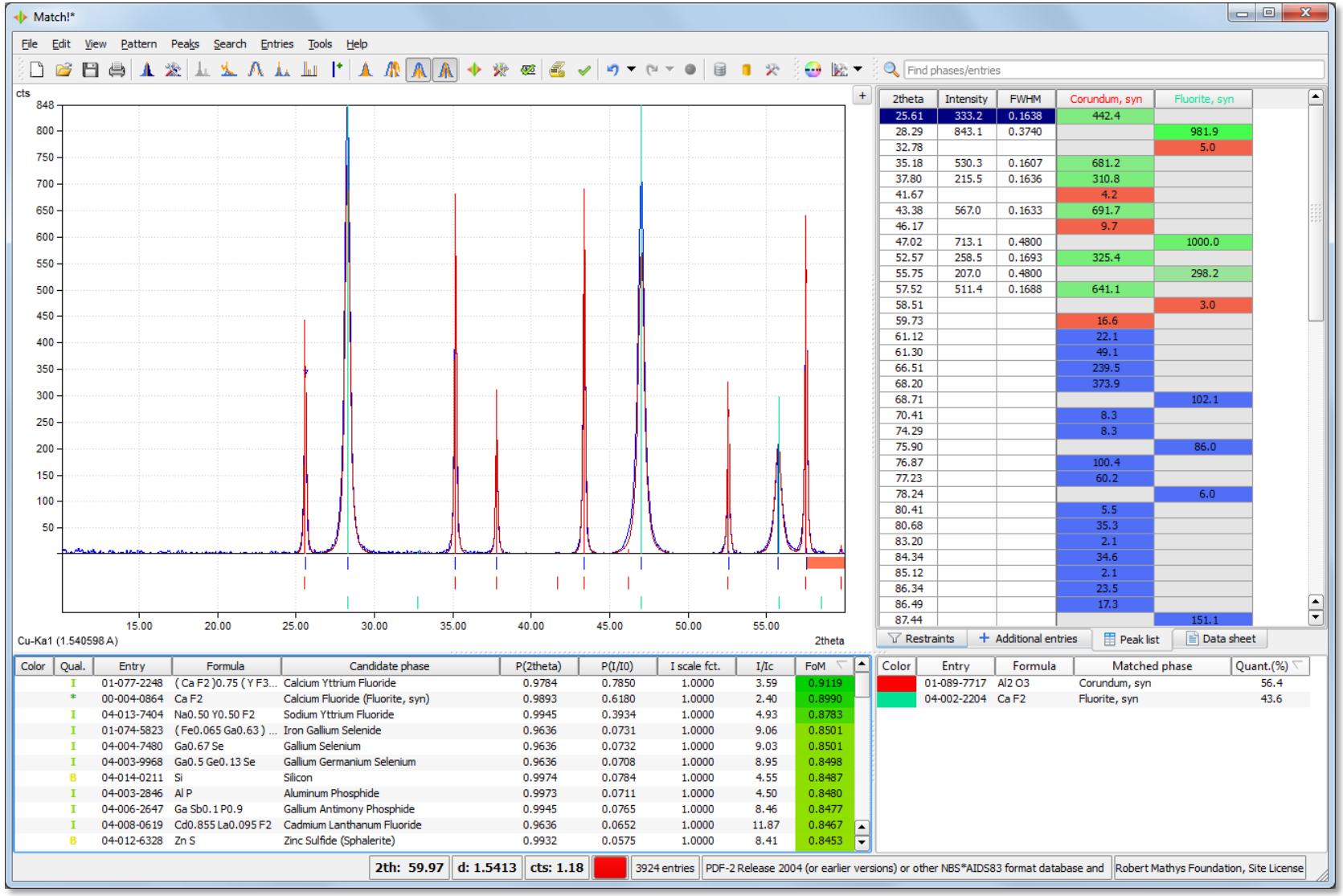




Usually sufficient for identification

Feature	Origin
Peak positions	- Symmetry of the unit cell (space group) - Dimensions of the unit cell
Relative peak intensities	- Coordinates of atoms in unit cell - Species of atoms
Absolute peak intensities	- Abundance of phase
Peak width	- Crystallite size - Stress/Strain in crystal lattice

Search-Match for Phase Identification



2theta	Intensity	FWHM	Corundum, syn	Fluorite, syn
25.61	333.2	0.1638	442.4	
28.29	843.1	0.3740		981.9
32.78				5.0
35.18	530.3	0.1607	681.2	
37.80	215.5	0.1636	310.8	
41.67			4.2	
43.38	567.0	0.1633	691.7	
46.17			9.7	
47.02	713.1	0.4800		1000.0
52.57	258.5	0.1693	325.4	
55.75	207.0	0.4800		298.2
57.52	511.4	0.1688	641.1	
58.51				3.0
59.73			16.6	
61.12			22.1	
61.30			49.1	
66.51			239.5	
68.20			373.9	
68.71				102.1
70.41			8.3	
74.29			8.3	
75.90				86.0
76.87			100.4	
77.23			60.2	
78.24				6.0
80.41			5.5	
80.68			35.3	
83.20			2.1	
84.34			34.6	
85.12			2.1	
86.34			23.5	
86.49			17.3	
87.44				151.1

Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM
	I	01-077-2248	(Ca F2)0.75 (Y F3...	Calcium Yttrium Fluoride	0.9784	0.7850	1.0000	3.59	0.9119
	*	00-004-0864	Ca F2	Calcium Fluoride (Fluorite, syn)	0.9893	0.6180	1.0000	2.40	0.8990
	I	04-013-7404	Na0.50 Y0.50 F2	Sodium Yttrium Fluoride	0.9945	0.3934	1.0000	4.93	0.8783
	I	01-074-5823	(Fe0.065 Ga0.63) ...	Iron Gallium Selenide	0.9636	0.0731	1.0000	9.06	0.8501
	I	04-004-7480	Ga0.67 Se	Gallium Selenium	0.9636	0.0732	1.0000	9.03	0.8501
	I	04-003-9968	Ga0.5 Ge0.13 Se	Gallium Germanium Selenium	0.9636	0.0708	1.0000	8.95	0.8498
	B	04-014-0211	Si	Silicon	0.9974	0.0784	1.0000	4.55	0.8487
	I	04-003-2846	Al P	Aluminum Phosphide	0.9973	0.0711	1.0000	4.50	0.8480
	I	04-006-2647	Ga Sb0.1 P0.9	Gallium Antimony Phosphide	0.9945	0.0765	1.0000	8.46	0.8477
	I	04-008-0619	Cd0.855 La0.095 F2	Cadmium Lanthanum Fluoride	0.9636	0.0652	1.0000	11.87	0.8467
	B	04-012-6328	Zn S	Zinc Sulfide (Sphalerite)	0.9932	0.0575	1.0000	8.41	0.8453

Color	Entry	Formula	Matched phase	Quant.(%)
	01-089-7717	Al2 O3	Corundum, syn	56.4
	04-002-2204	Ca F2	Fluorite, syn	43.6

Rietveld Refinement

For more than just identification:

Rietveld refinement

Prof. Hugo Rietveld

Extracts much more information from powder XRD data:

- Unit cell dimensions
- Phase quantities
- Crystallite sizes / shapes
- Atomic coordinates / Bond lengths
- Micro-strain in crystal lattice
- Texture effects
- Substitutions / Vacancies

No phase identification!

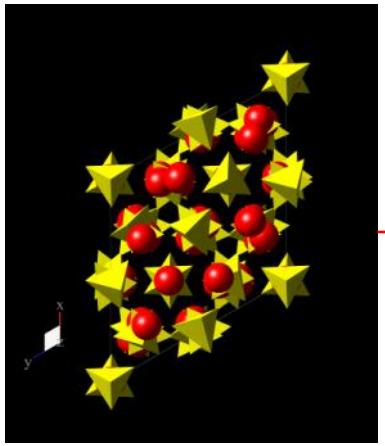
Identify your phases first
(unknown phase → no Rietveld refinement)

No structure solution
(just structure refinement)

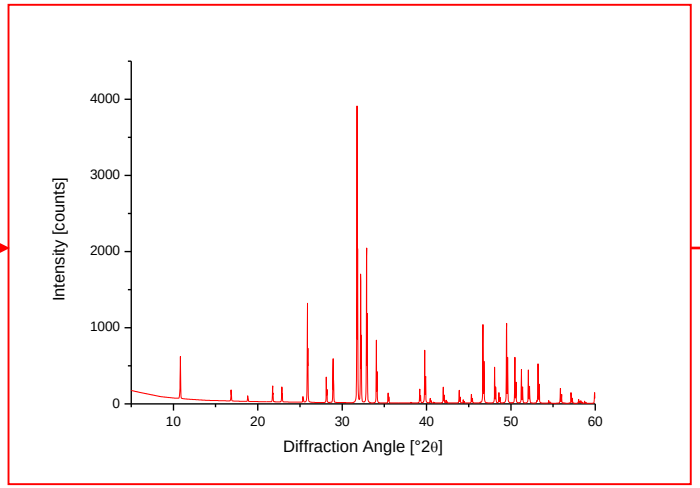
Needs excellent data quality!

Rietveld Refinement

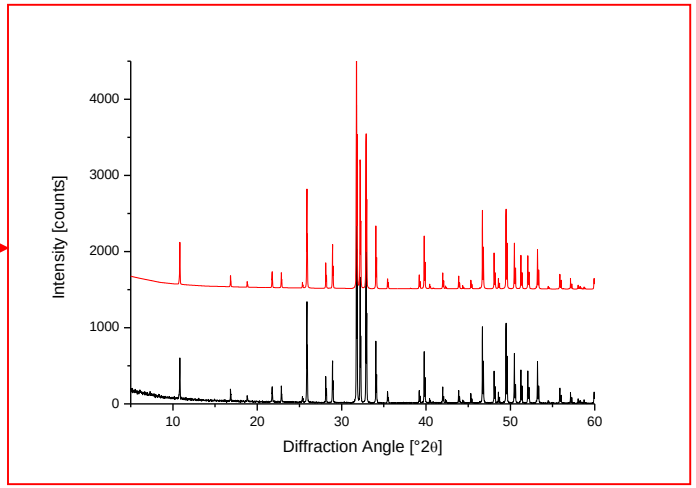
Known structure model



Calculate theoretical diffraction pattern



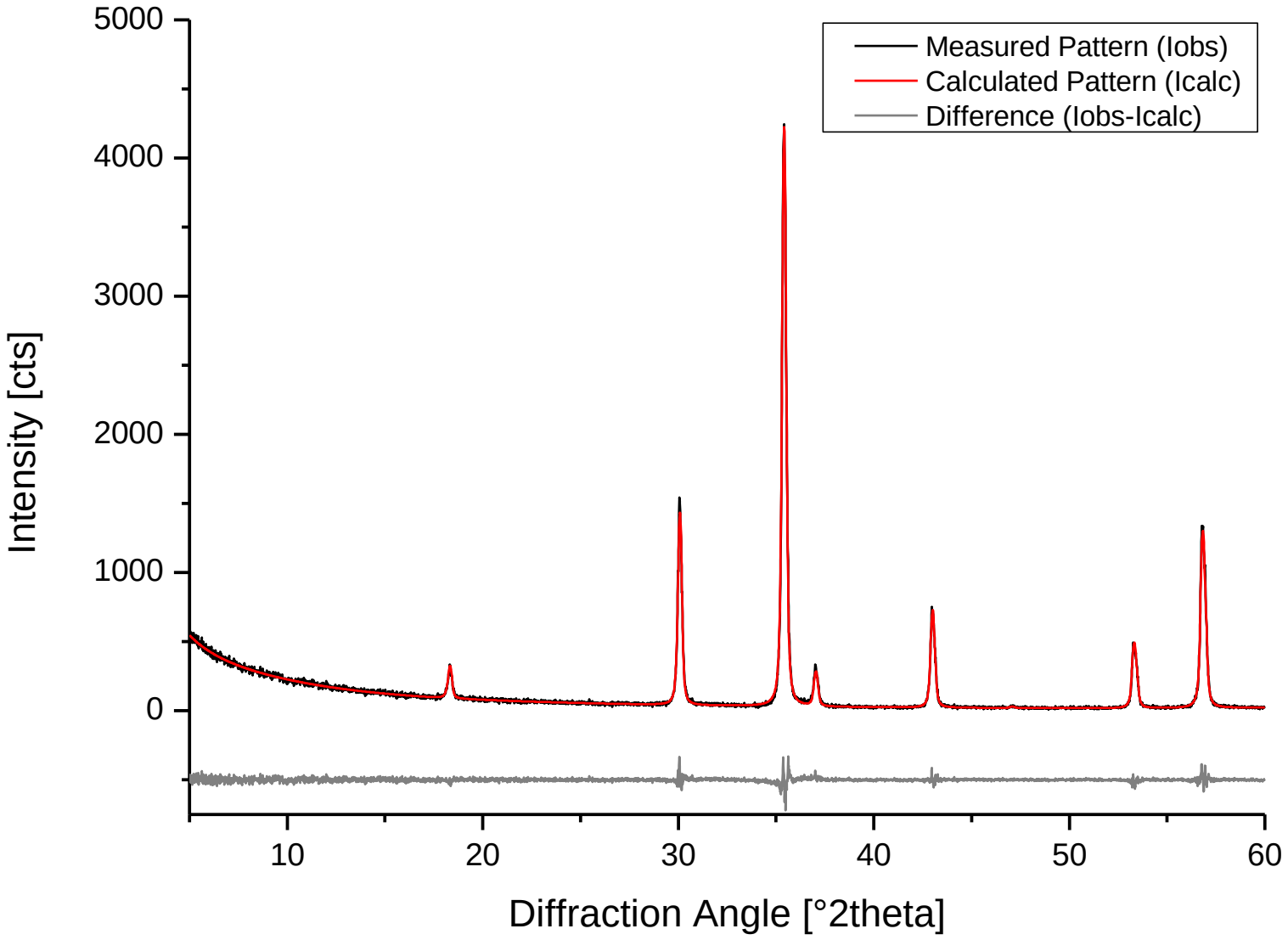
Compare with measured pattern



Optimize structure model, repeat calculation

Minimize differences between calculated and observed pattern by least-squares method

Rietveld Refinement



Rietveld Software Packages

Academic Software:

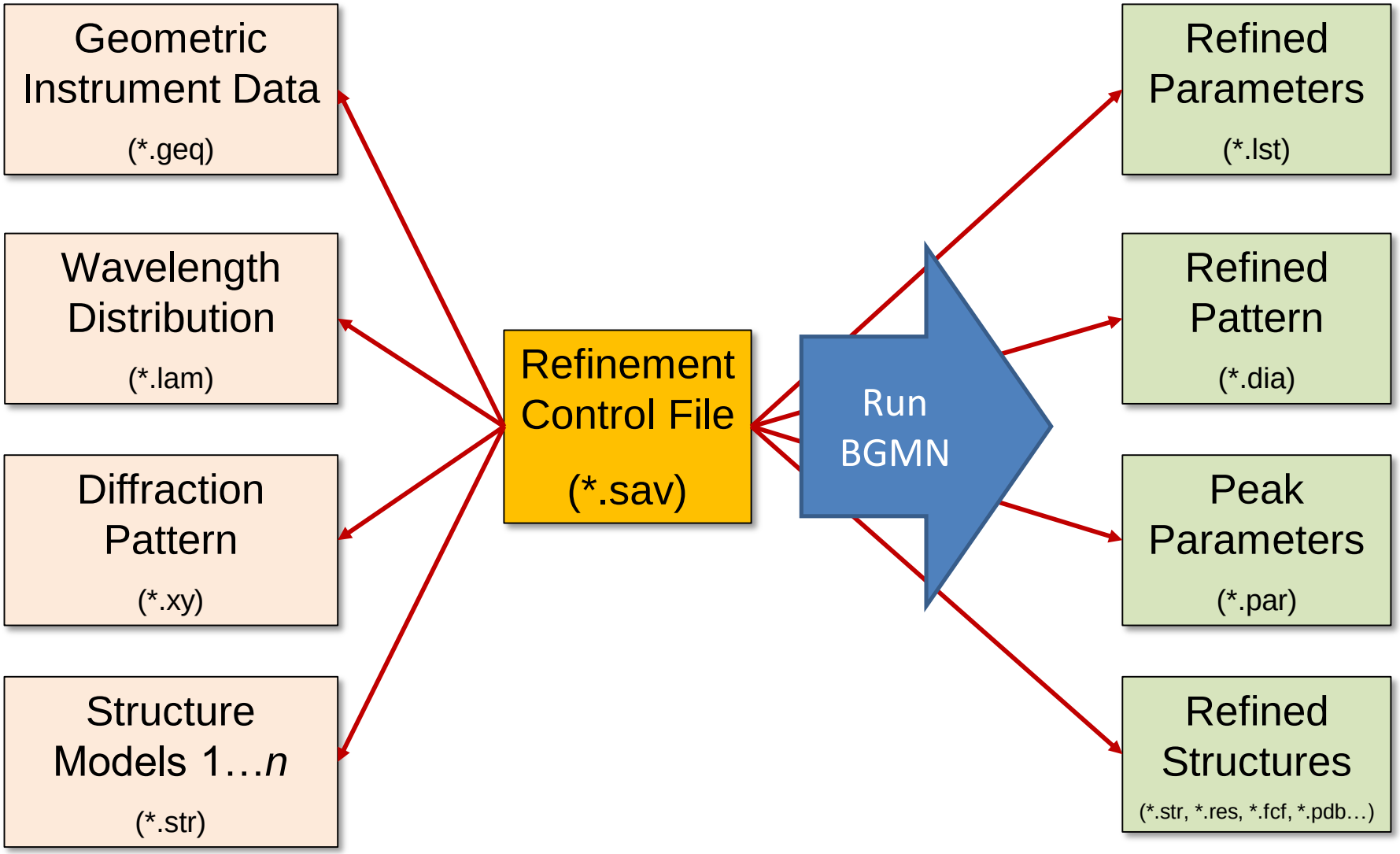
- Fullprof
- GSAS
- BGMN
- Maud
- Brass
- … many more[1)]

Commercial Software:

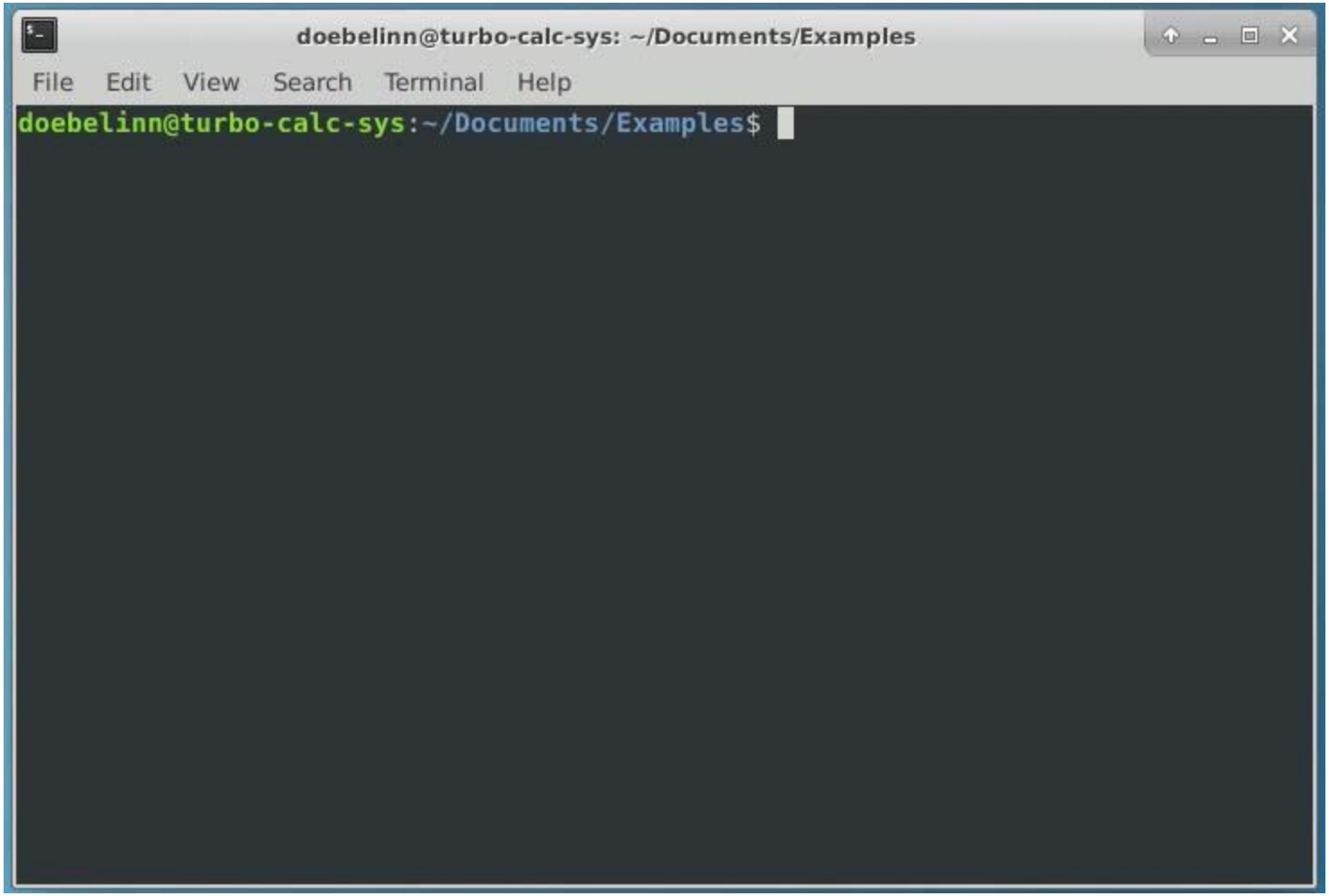
- HighScore+ (PANalytical)
- Topas (Bruker)
- Autoquan (GE)
- PDXL (Rigaku)
- Jade (MDI)
- WinX^{POW} (Stoe)

1) http://www.ccp14.ac.uk/solution/rietveld_software/index.html

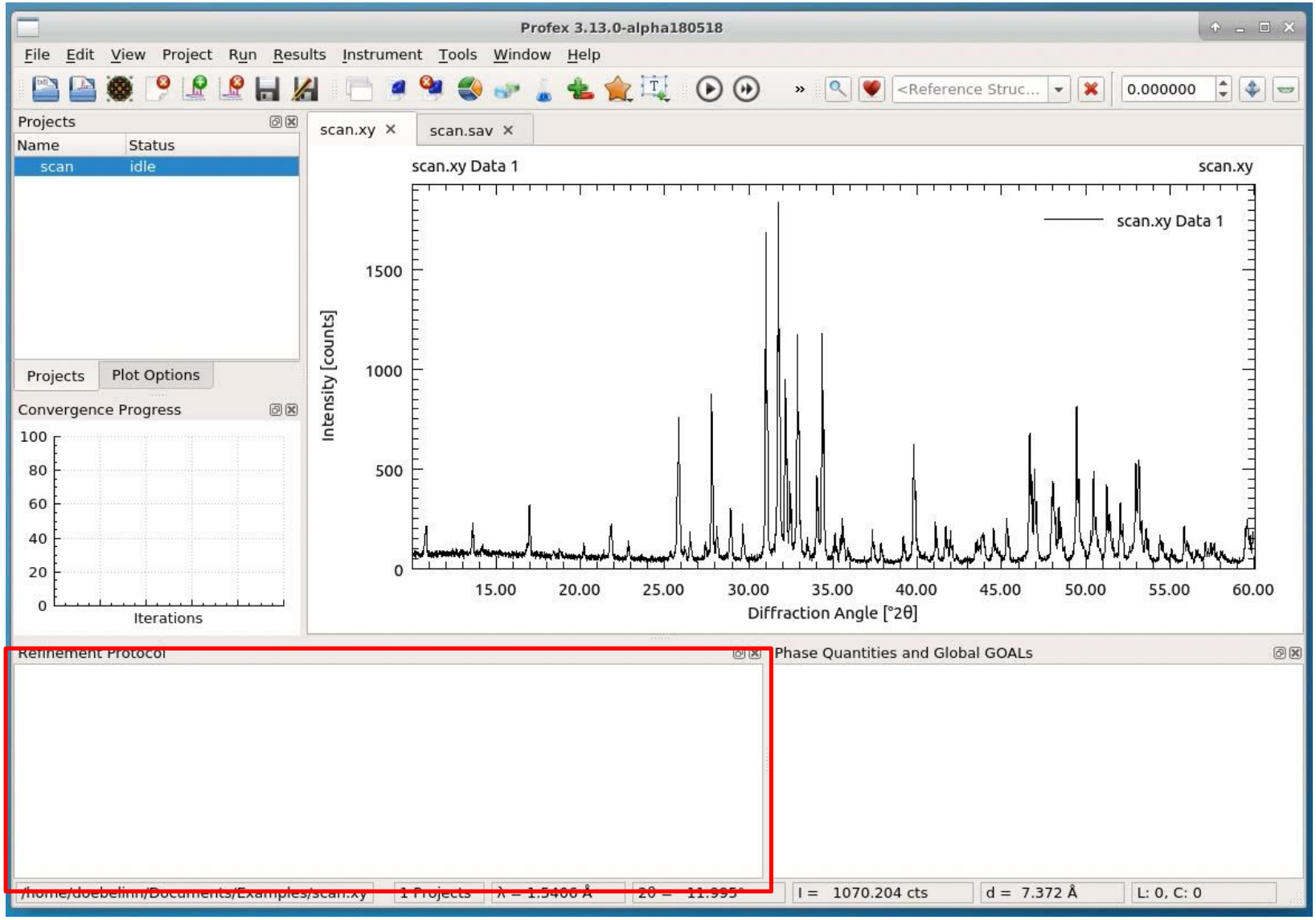
BGMN: Based on Text Files



BGMN


doebelinn@turbo-calc-sys: ~/Documents/Examples
File Edit View Search Terminal Help
doebelinn@turbo-calc-sys:~/Documents/Examples$

Profex: A Graphical User Interface for BGMN

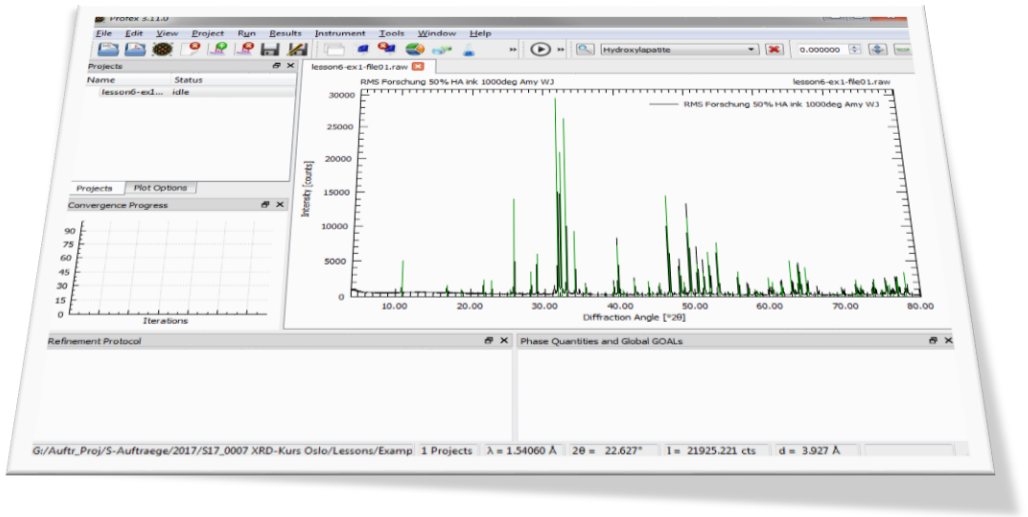


Profex: A Graphical User Interface for BGMN

Developer:	Nicola Döbelin (private)
License:	GPL v2 or later (open source)
Founded in:	2003
Platforms:	Windows 7 / 8 / 8.1 / 10 Linux Mac OS X 10.9 -10.13 (64bit)
Rietveld Backends:	BGMN, Fullprof.2k
Website:	http://profex.doebelin.org
Current stable version:	3.13.0

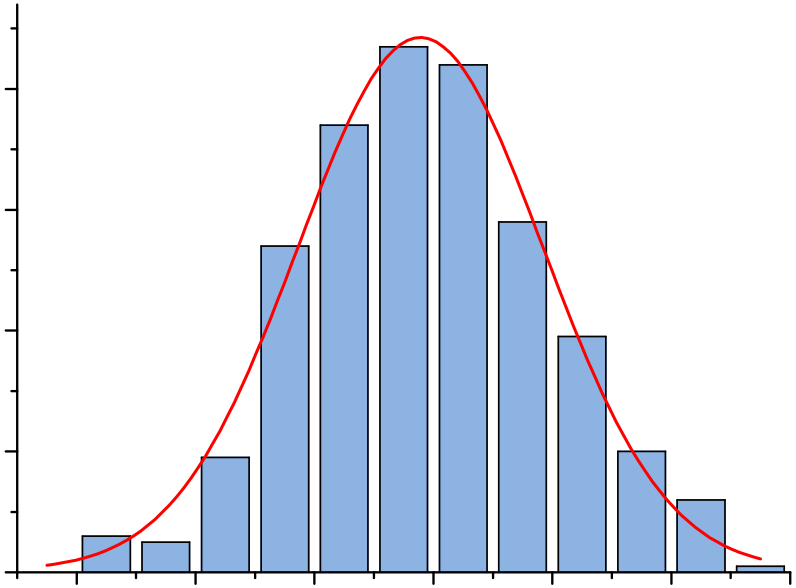
Profex Key Features

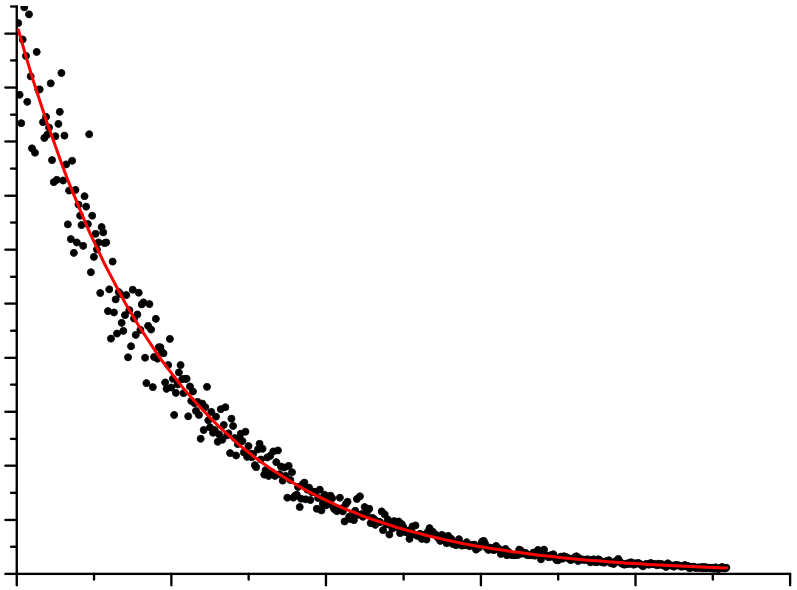
- Create and manage refinement projects
- Convert raw data files for BGMN
- Export results and graphs
- Batch refinements
- Structure and Instrument file repositories
- + many more…



Fitting Data

Fitting experimental data requires an adequate mathematical model

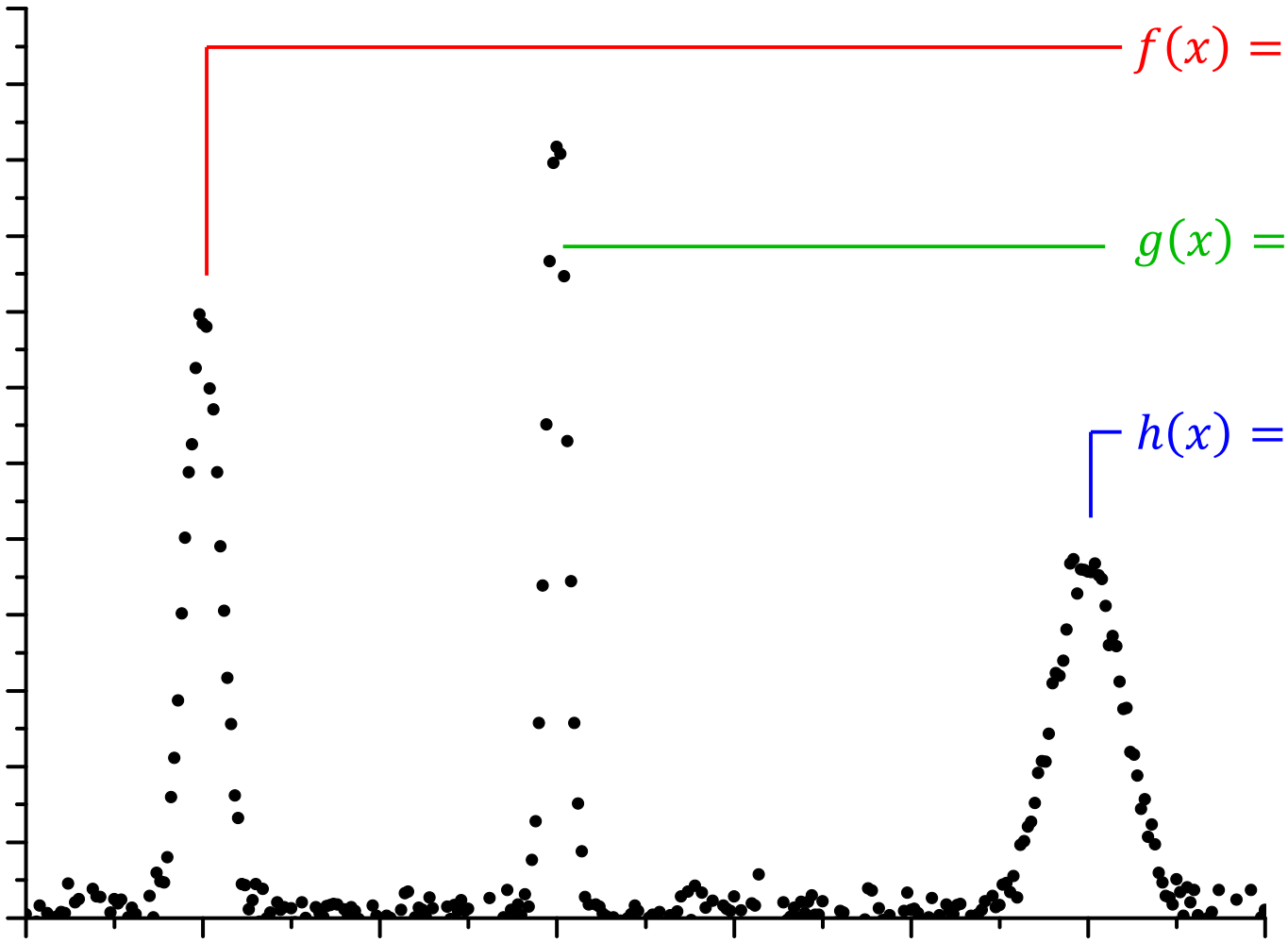




$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

$$f(x) = a \cdot e^{-\frac{x}{t}} + y_0$$

Fitting Data

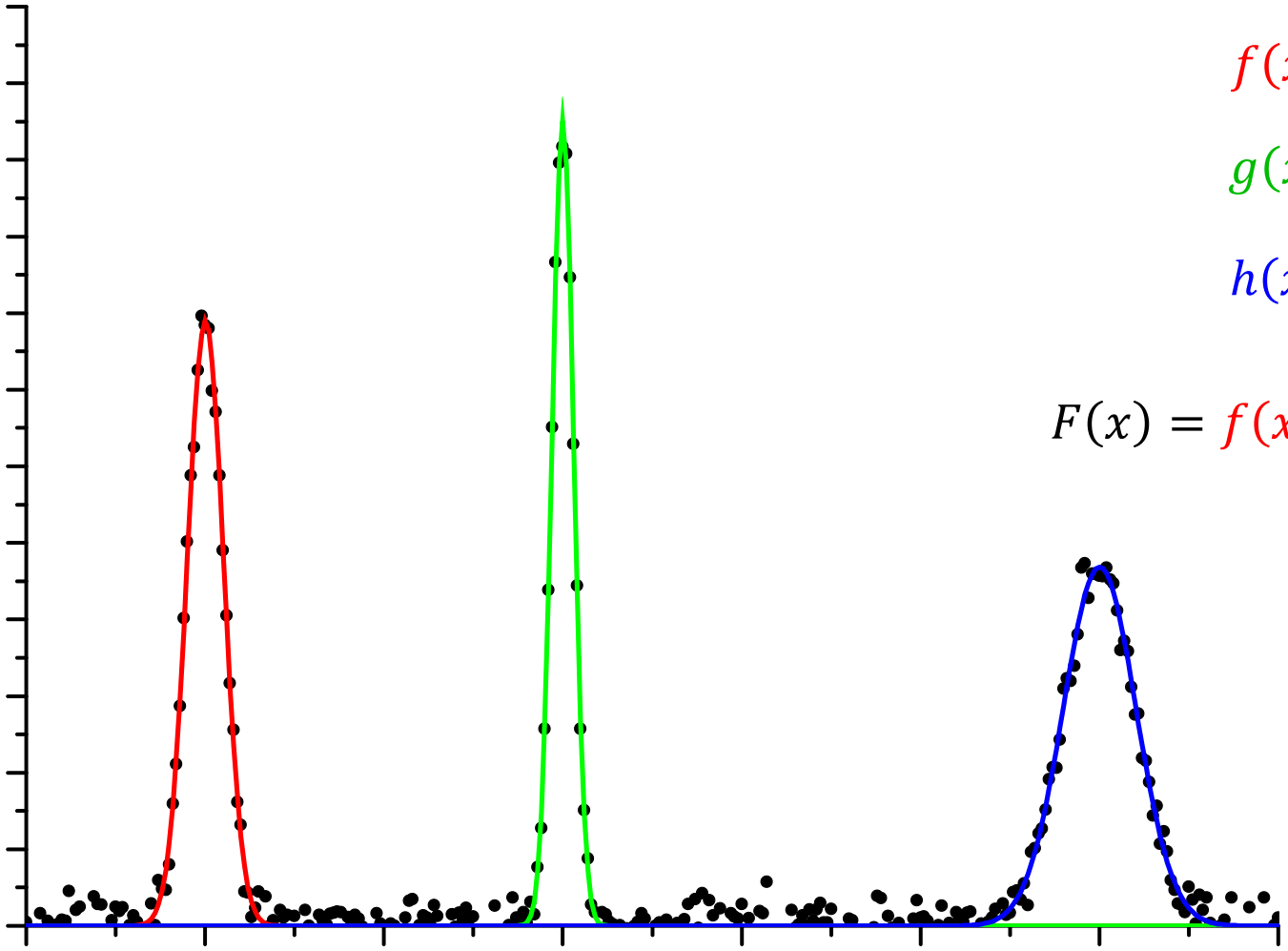


$$f(x) = \frac{A_1}{\sigma_1\sqrt{2\pi}} \cdot e^{-\frac{(x-\mu_1)^2}{2\sigma_1^2}}$$

$$g(x) = \frac{A_2}{\sigma_2\sqrt{2\pi}} \cdot e^{-\frac{(x-\mu_2)^2}{2\sigma_2^2}}$$

$$h(x) = \frac{A_3}{\sigma_3\sqrt{2\pi}} \cdot e^{-\frac{(x-\mu_3)^2}{2\sigma_3^2}}$$

Fitting Data



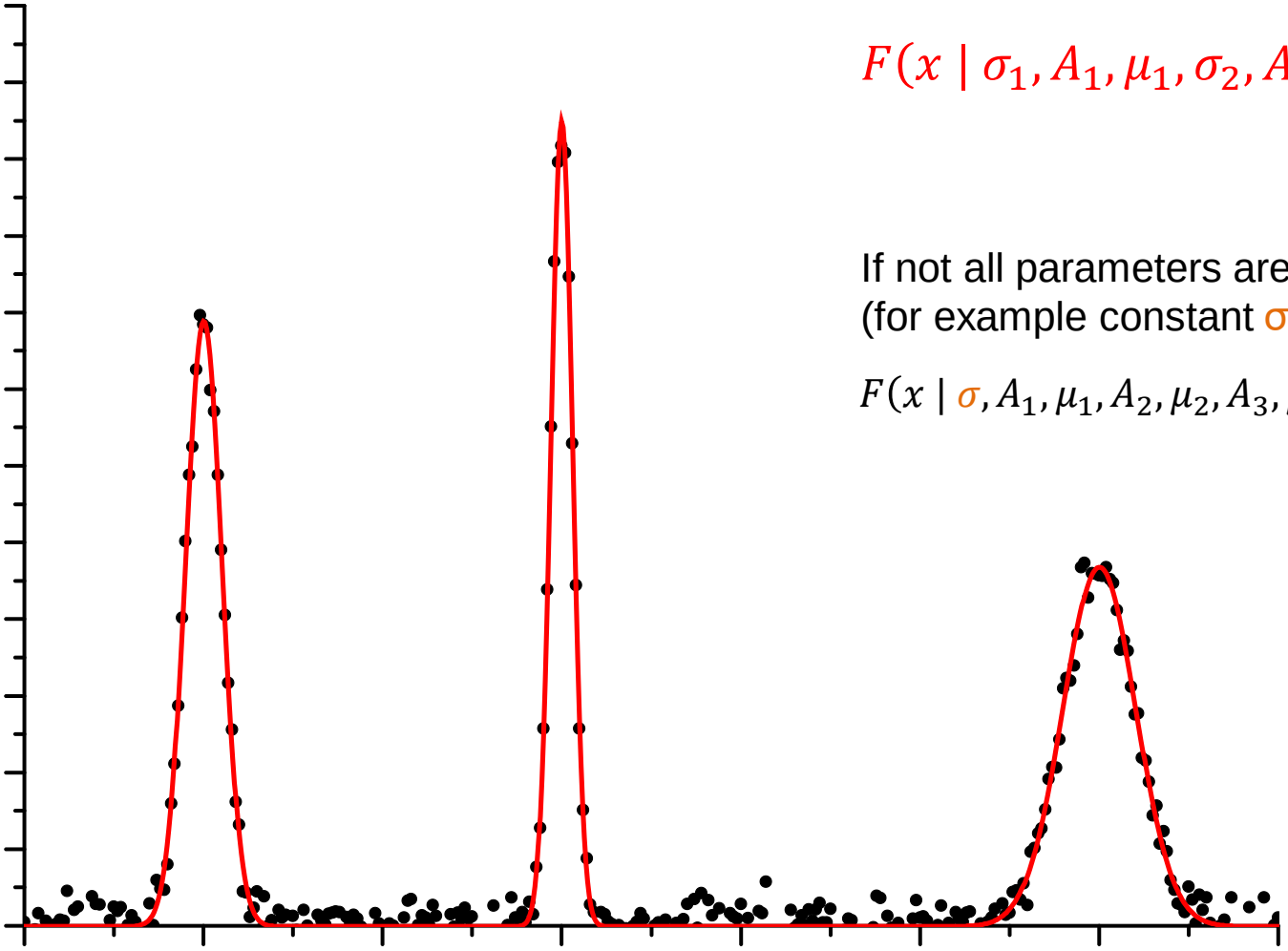
$$f(x \mid \sigma_1, A_1, \mu_1)$$

$$g(x \mid \sigma_2, A_2, \mu_2)$$

$$h(x \mid \sigma_3, A_3, \mu_3)$$

$$F(x) = f(x) + g(x) + h(x)$$

Fitting Data

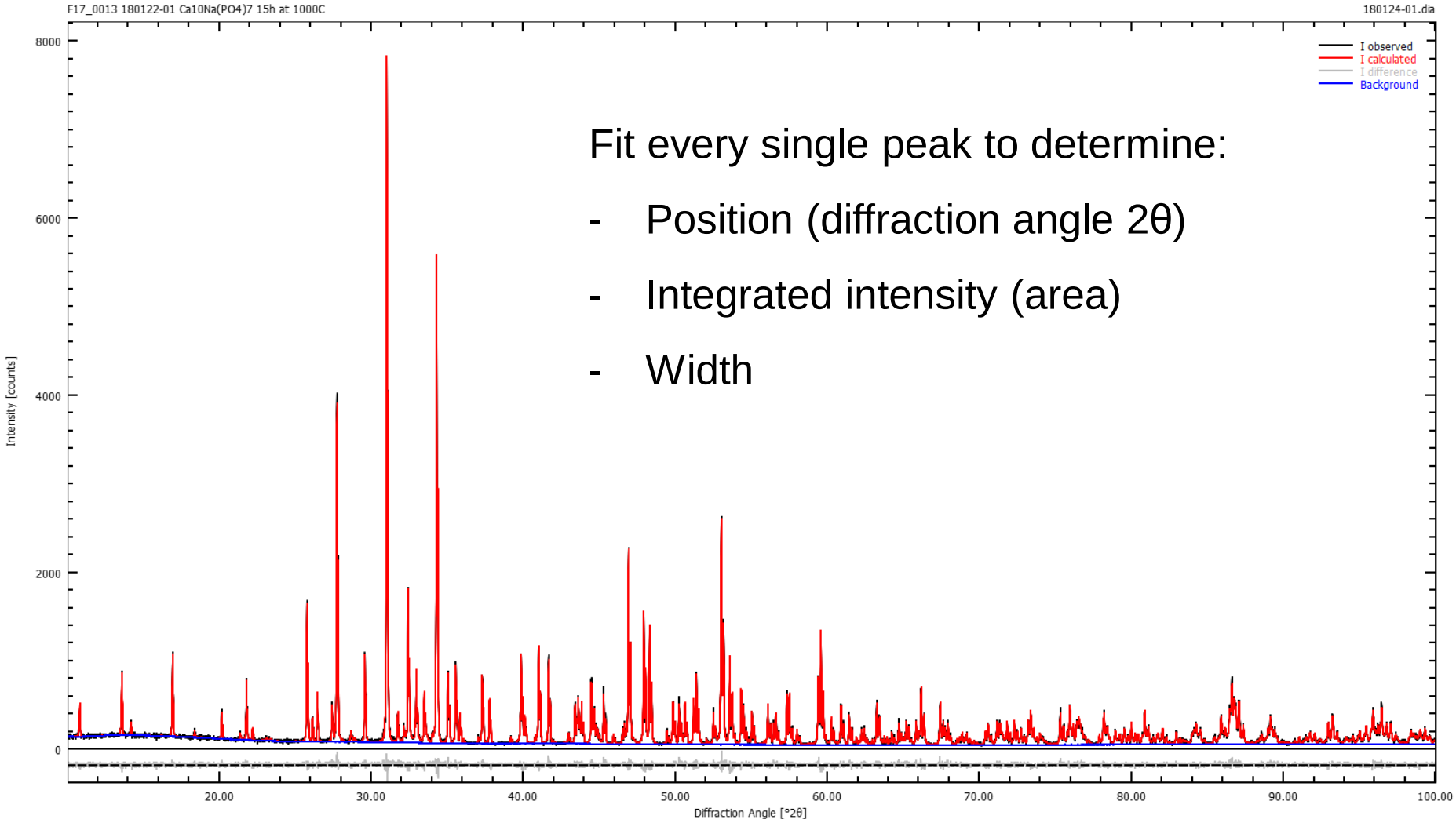


$$F(x \mid \sigma_1, A_1, \mu_1, \sigma_2, A_2, \mu_2, \sigma_3, A_3, \mu_3)$$

If not all parameters are independent, (for example constant σ):

$$F(x \mid \sigma, A_1, \mu_1, A_2, \mu_2, A_3, \mu_3)$$

Fitting Diffraction Patterns



Fit every single peak to determine:

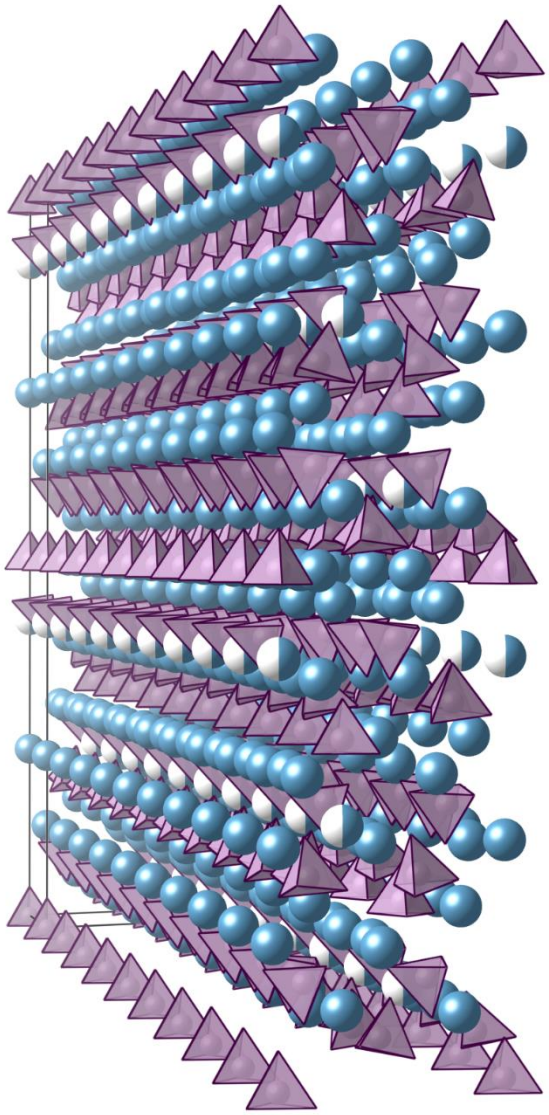
- Position (diffraction angle 2θ)
- Integrated intensity (area)
- Width

Fitting Diffraction Patterns

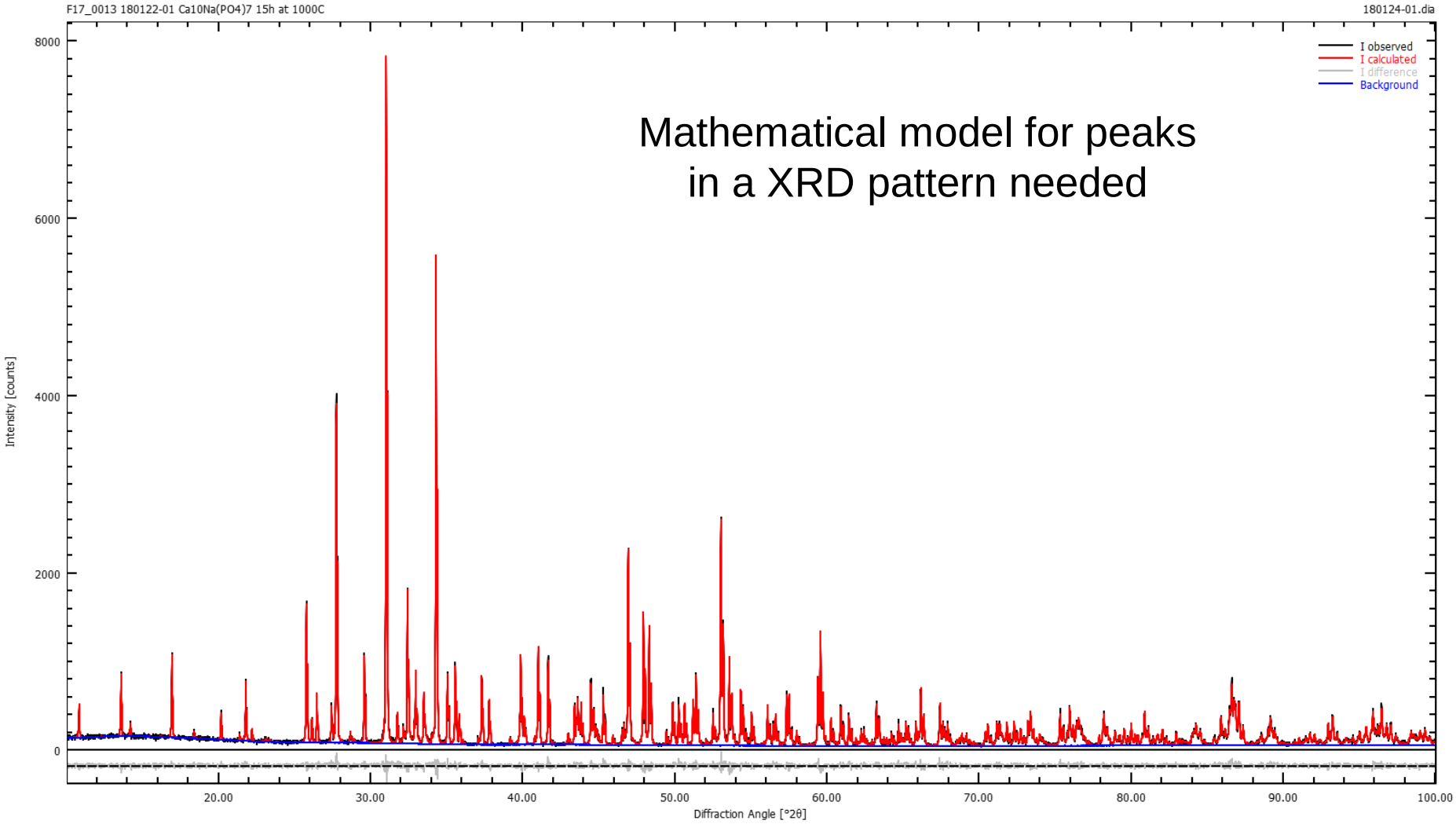
- Diffraction angle → lattice plane spacing *d*
  - Lattice type
  - Space group
  - Unit cell dimensions

- Intensity → Structure factor F_{hkl}
  - Atomic species
  - Fractional coordinates
  - Site occupancies
  - Thermal vibration
  - Phase quantity

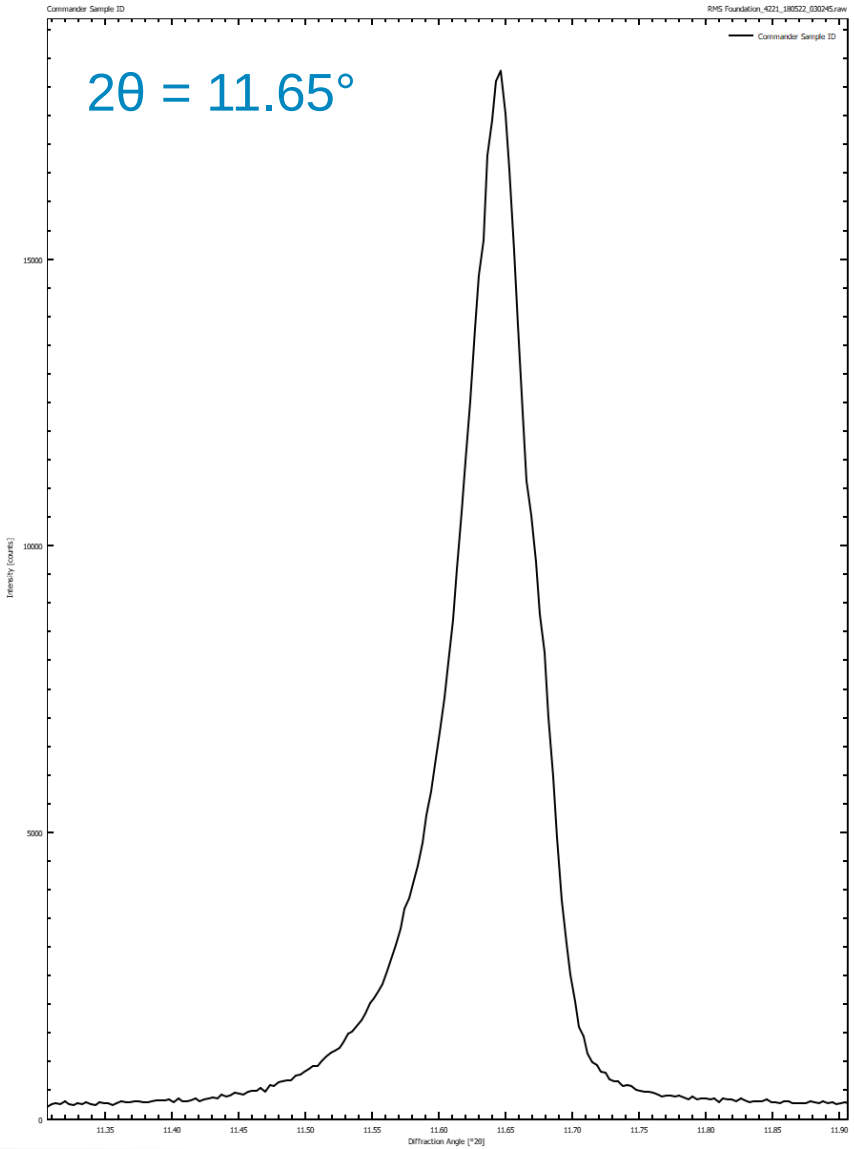
- Width
  - Crystallite size
  - Micro-strain

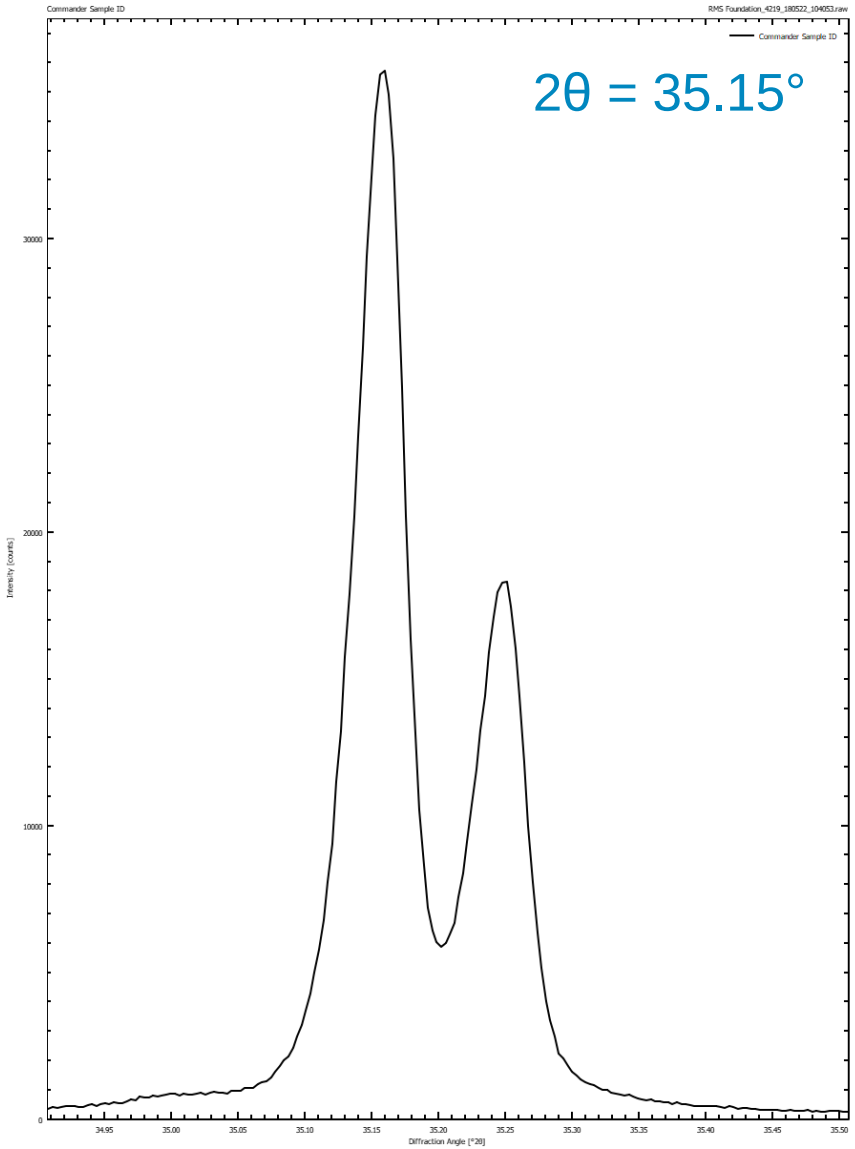


Fitting Diffraction Patterns



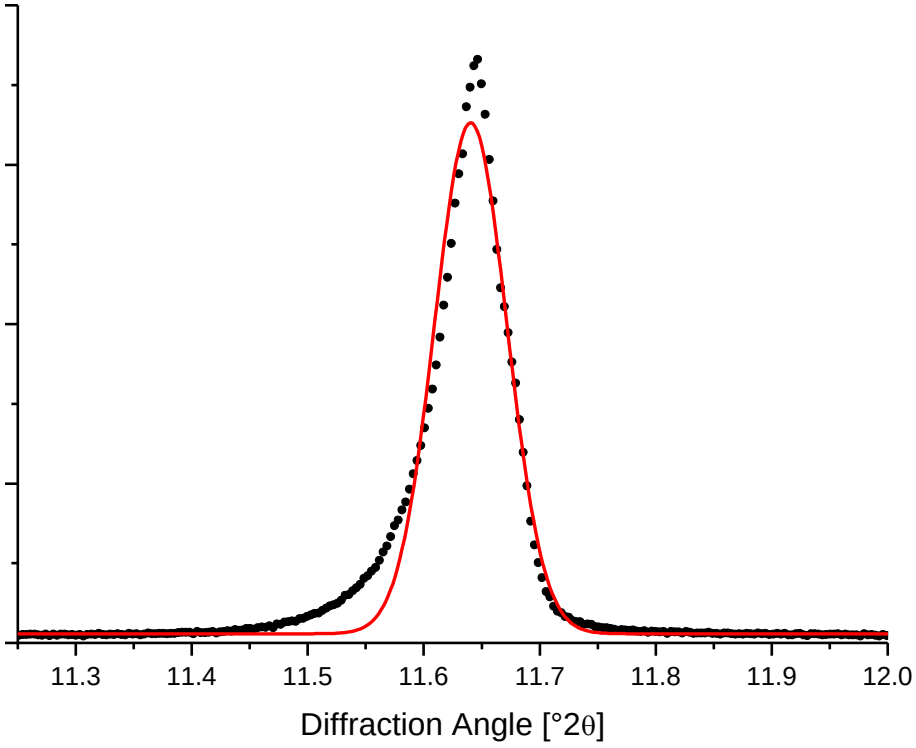
Fitting Diffraction Patterns

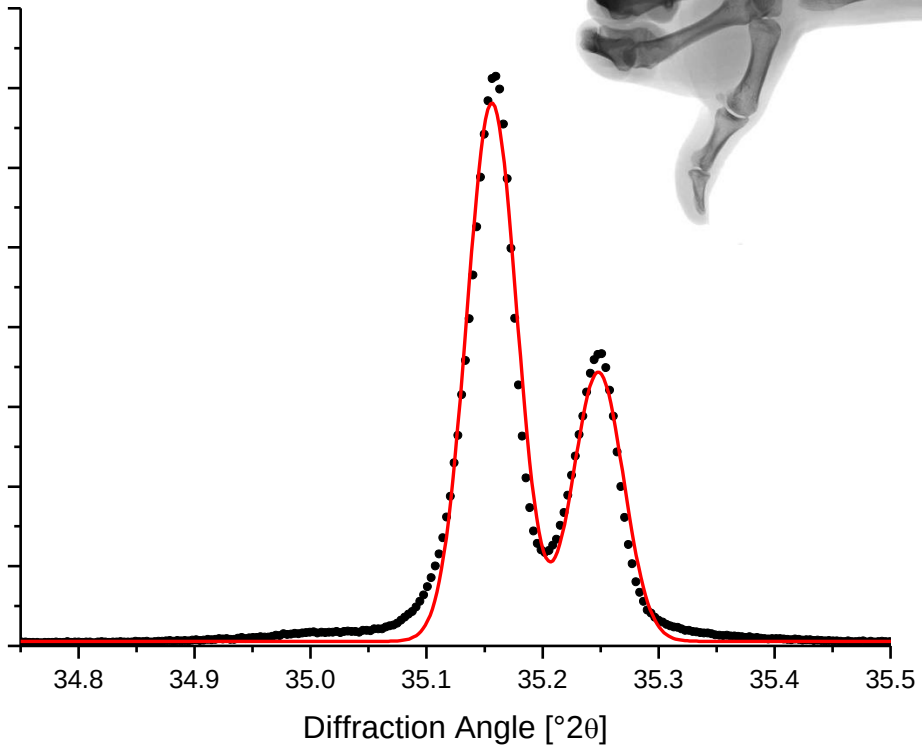




Modelling the Peak Profile

Two Gaussian functions





Modelling the Peak Profile

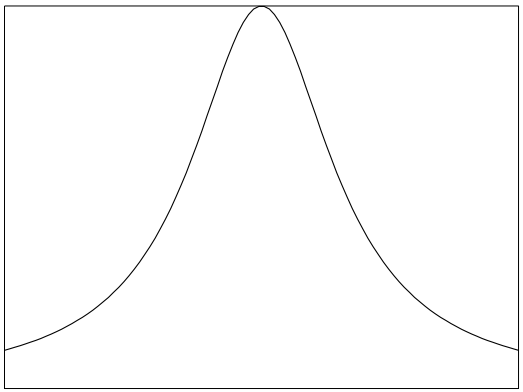
Traditional («Rietveld») Approach:

Pseudo-Voigt curves for $K\alpha_1$, $K\alpha_2$ and $K\beta$

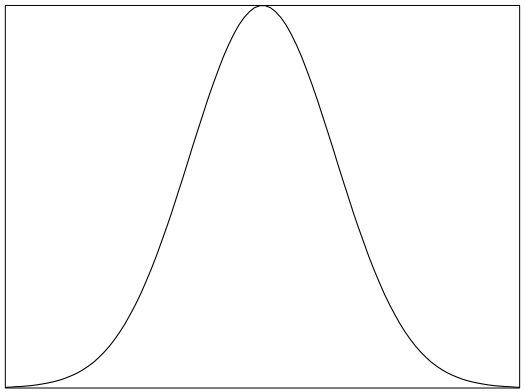
$$V_P(x) = n \cdot L(x) + (1 - n) \cdot G(x)$$

Lorentzian

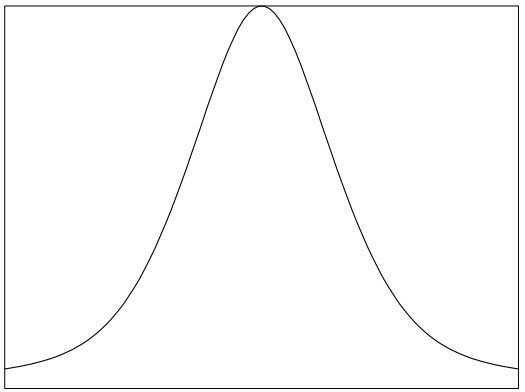
Gaussian



Lorentzian (ω = 1.0)



Gaussian (ω = 1.0)



Pseudo-Voigt (n = 0.5)

Profile functions in FullProf.2k

Npr – Defaut profile to be used

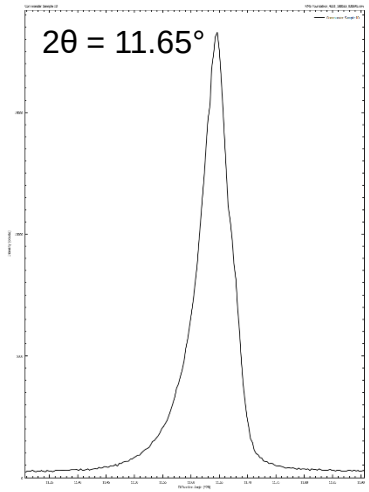
Default value for selection of a normalised peak shape function. Particular values can be given for each phase, in that case the local value is used.

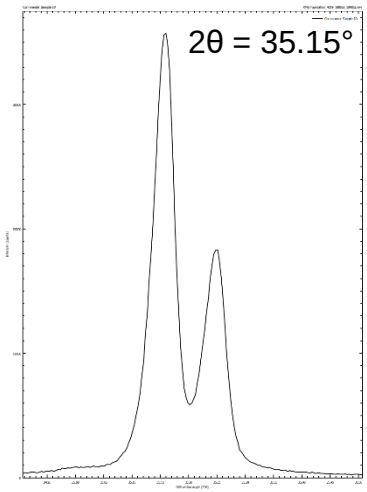
=0	Gaussian.
=1	Cauchy (Lorentzian).
=2	Modified 1 Lorentzian.
=3	Modified 2 Lorentzian.
=4	Tripled pseudo-Voigt.
=5	pseudo-Voigt.
=6	Pearson VII.
=7	Thompson-Cox-Hastings pseudo-Voigt convoluted with axial divergence asymmetry function (Finger, Cox & Jephcoat, J. Appl. Cryst. 27, 892, 1994).
=8	Numerical profile given in CODFIL.shp or in GLOBAL.shp.
=9	T.O.F. Convolution pseudo-Voigt with back-to-back exponential functions.
=10	T.O.F. Same as 9 but a different dependence of TOF versus d-spacing.
=11	Split pseudo-Voigt function.
=12	Pseudo-Voigt function convoluted with axial divergence asymmetry function.
=13	T.O.F. Pseudo-Voigt function convoluted with Ikeda-Carpenter function.

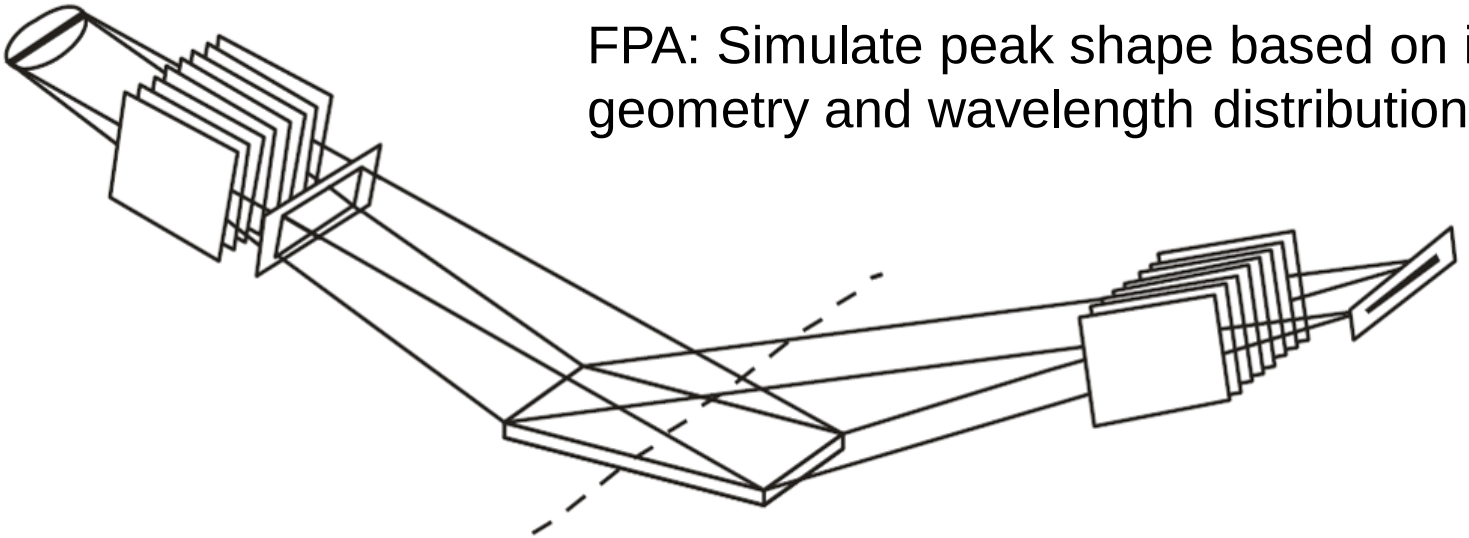
Alternative: Fundamental Parameters Approach (FPA)

Origin of peak shape features:

- Wavelength distribution (radiation spectrum)
- Instrument configuration





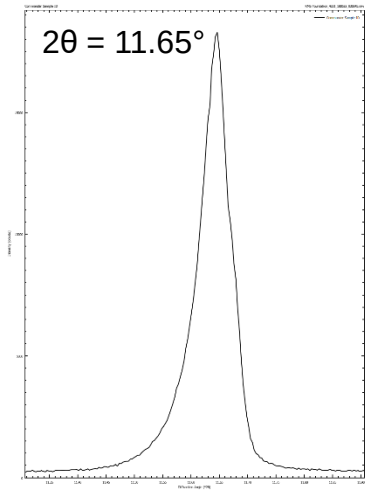


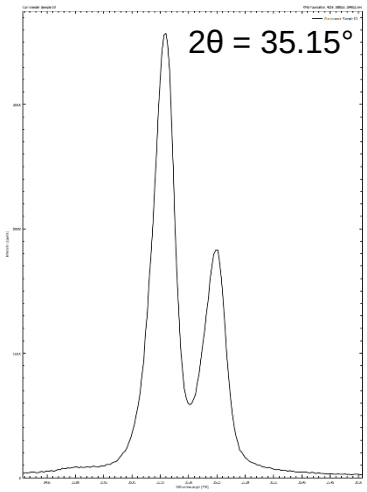
FPA: Simulate peak shape based on instrument geometry and wavelength distribution

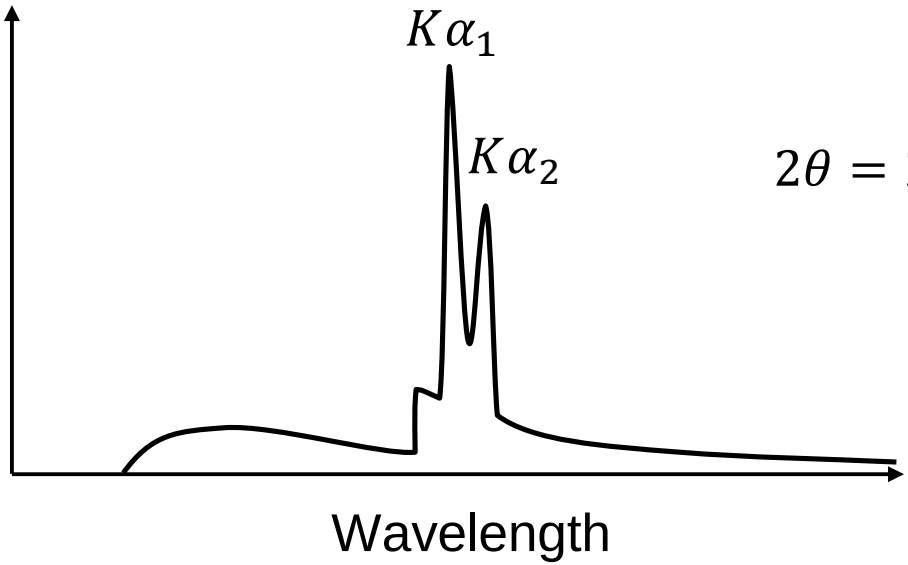
FPA: Wavelength Contribution

Origin of peak shape features:

- **Wavelength distribution (radiation spectrum)**
- Instrument configuration



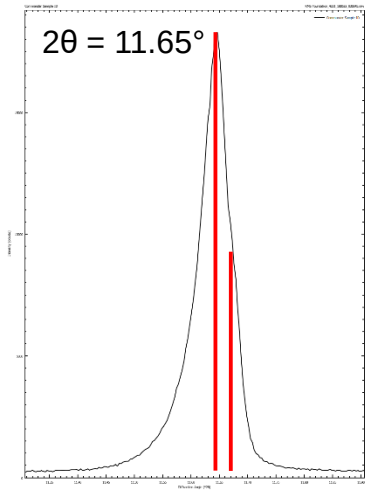


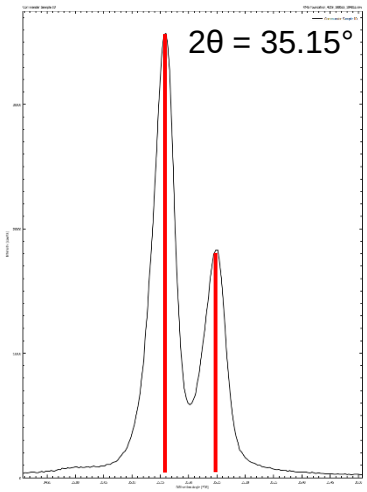


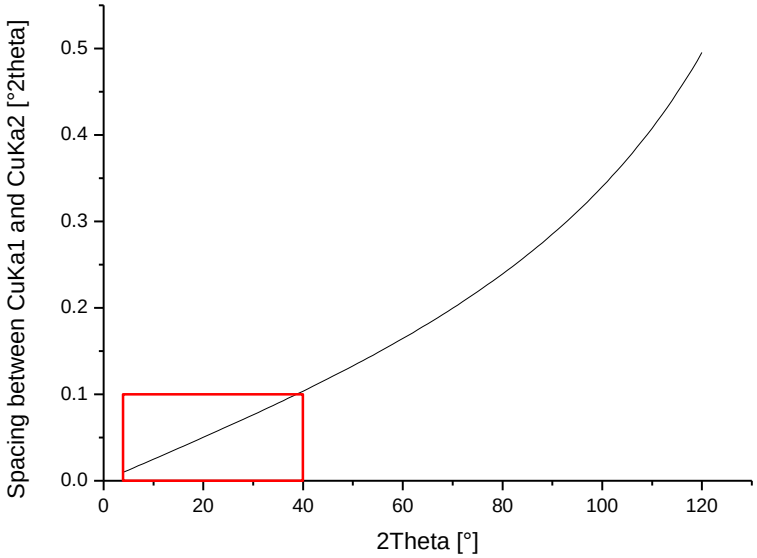
$$2\theta = 2 \cdot \mathrm{asin}\left(\frac{\lambda}{2d}\right)$$

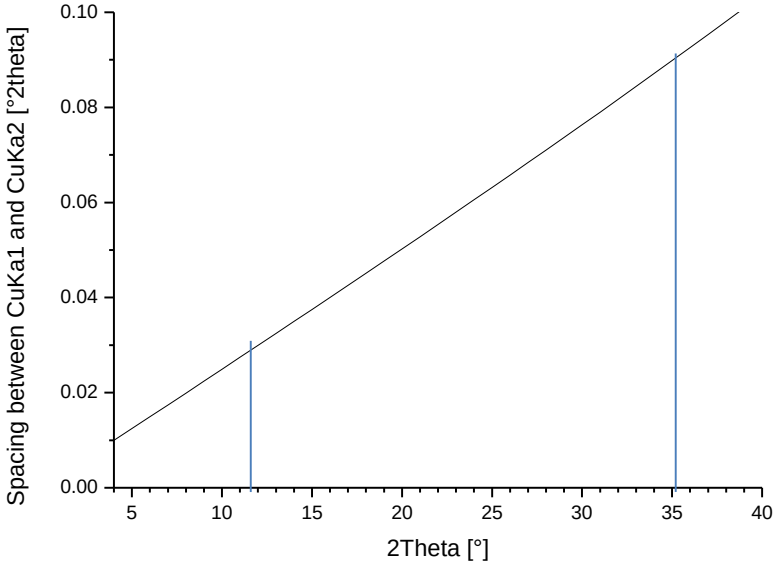
FPA: Wavelength Contribution

$$2\theta = 2 \cdot \operatorname{asin}\left(\frac{\lambda}{2d}\right)$$





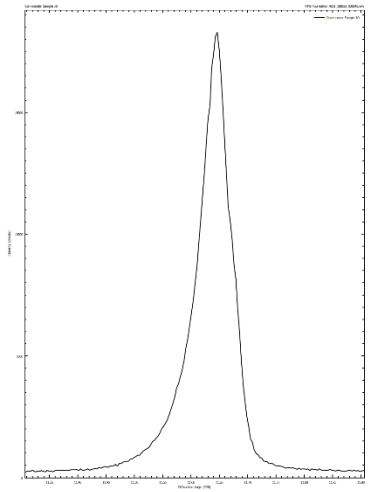


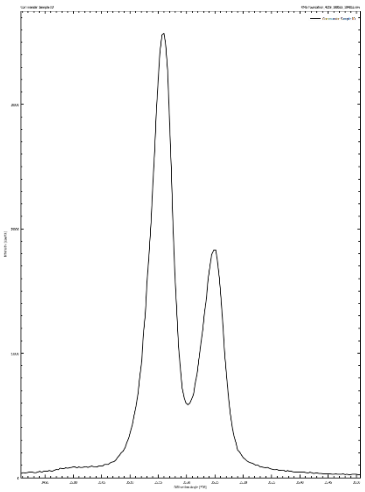


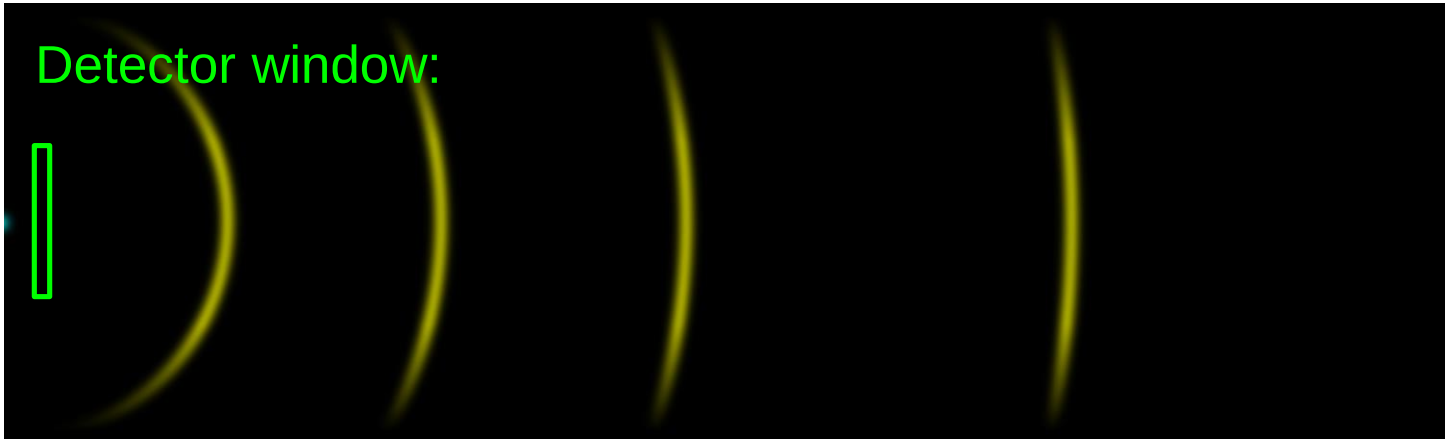
FPA: Instrument Contribution

Origin of peak shape features:

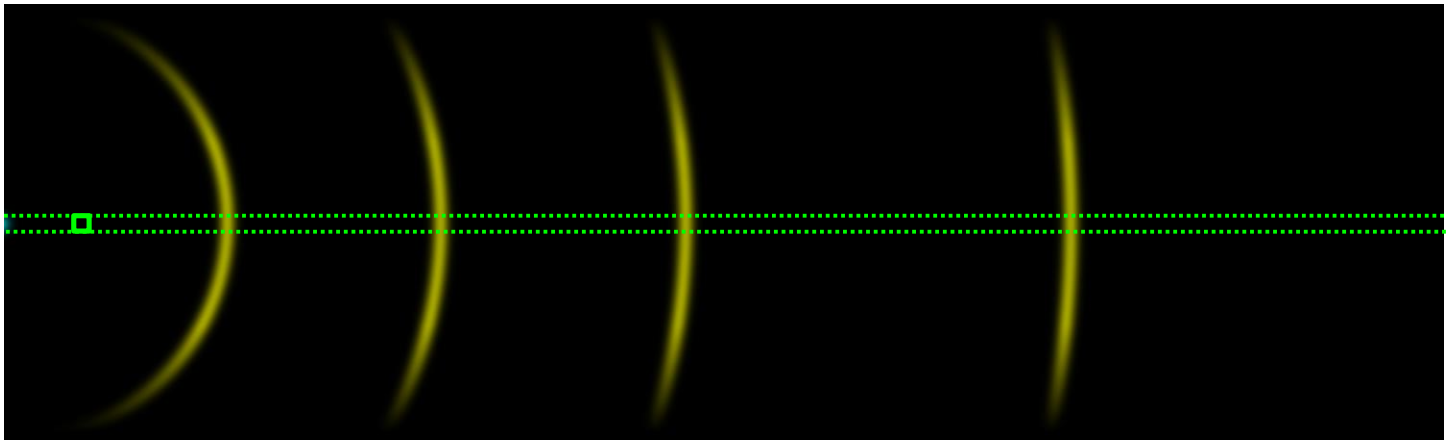
- Wavelength distribution (radiation spectrum)
- **Instrument configuration**

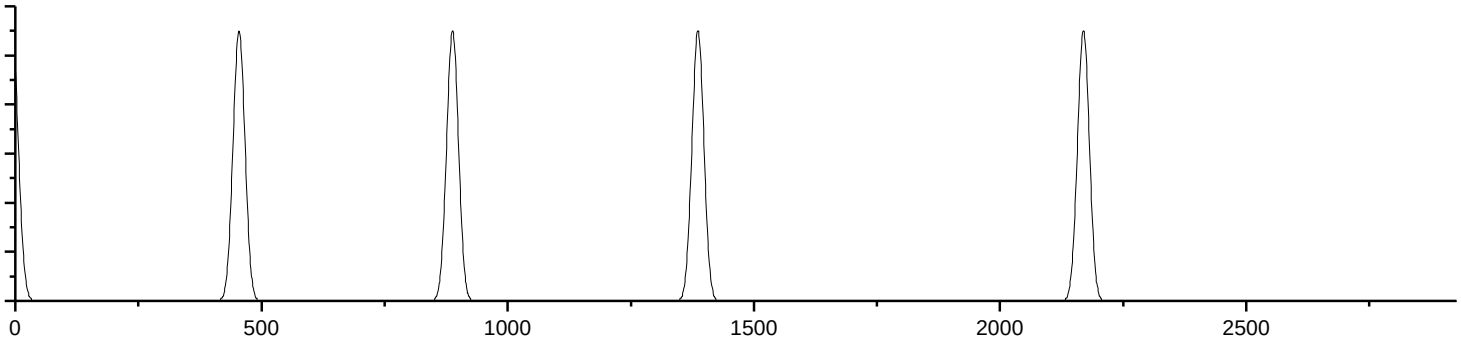




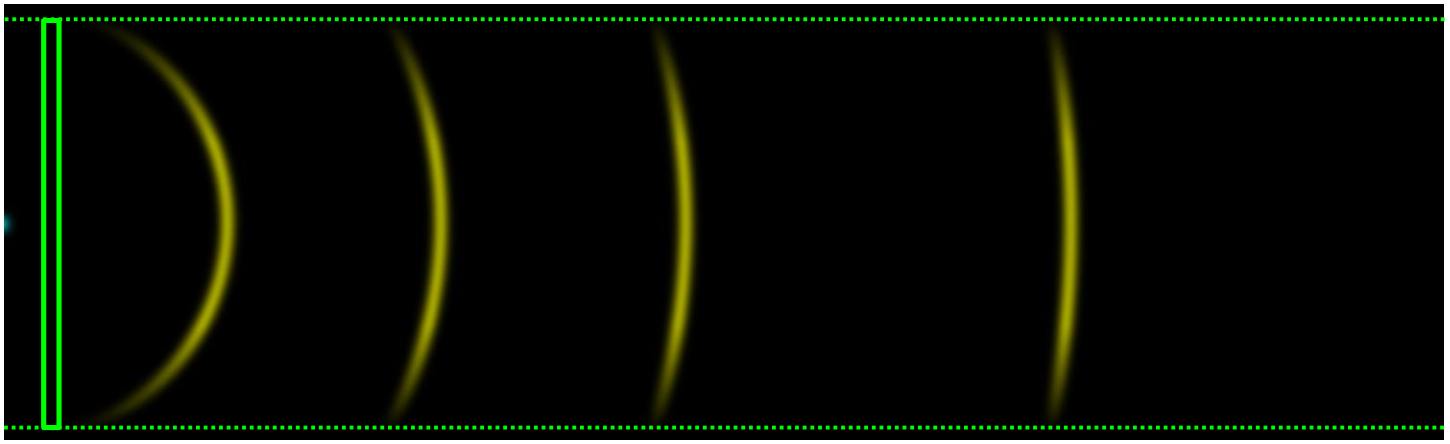


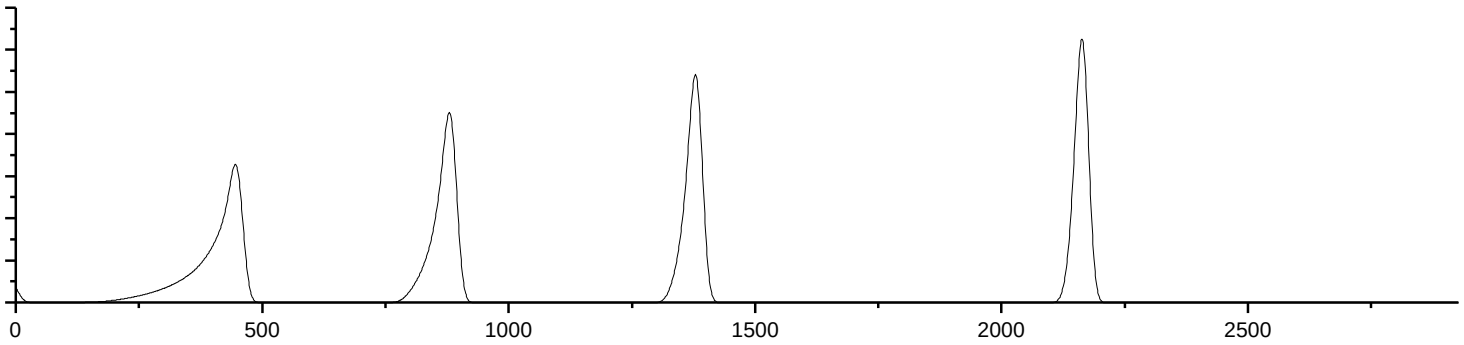
FPA: Instrument Contribution





FPA: Instrument Contribution

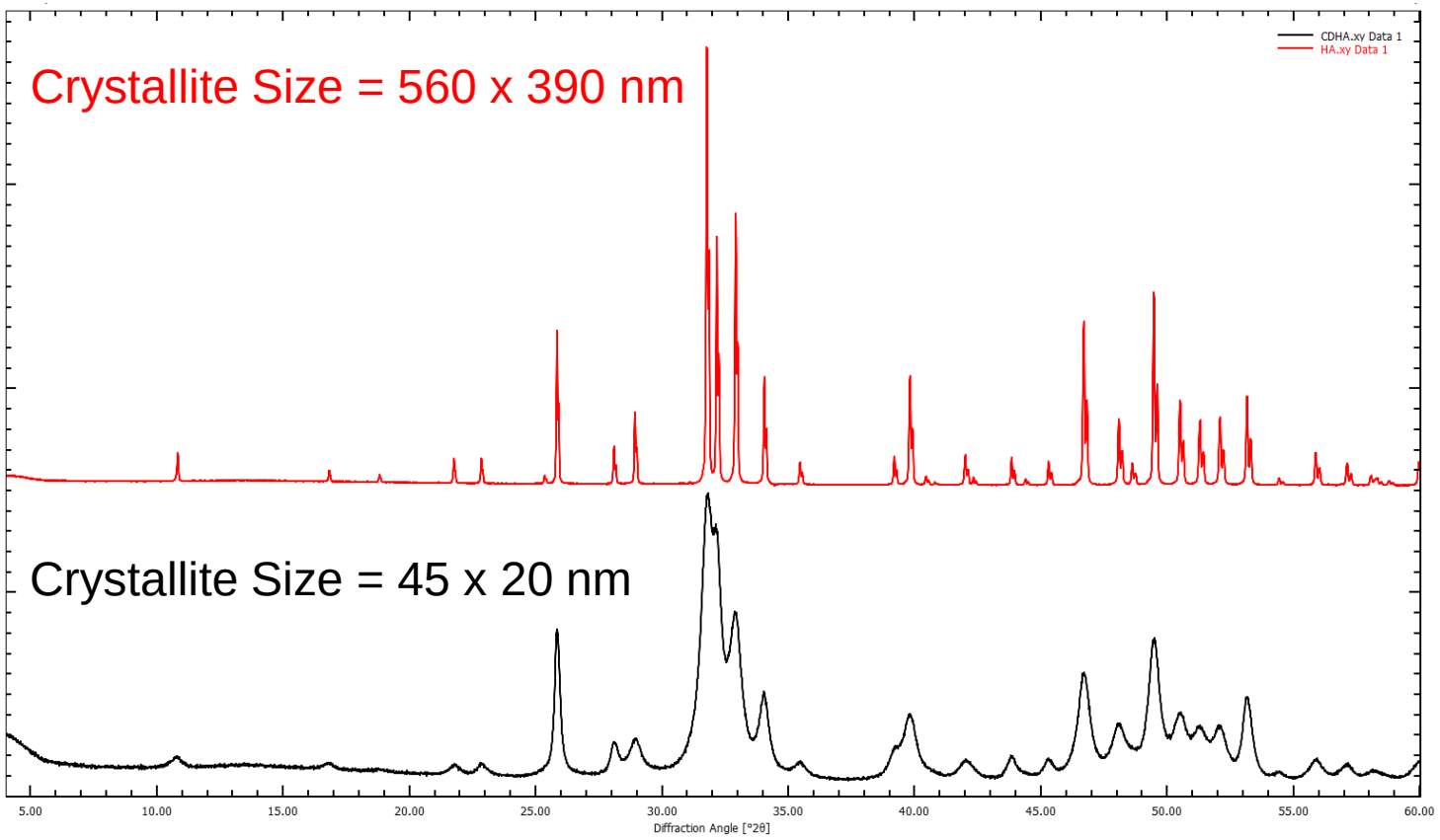




FPA: Sample Contribution

The same crystalline phase, same instrument configuration

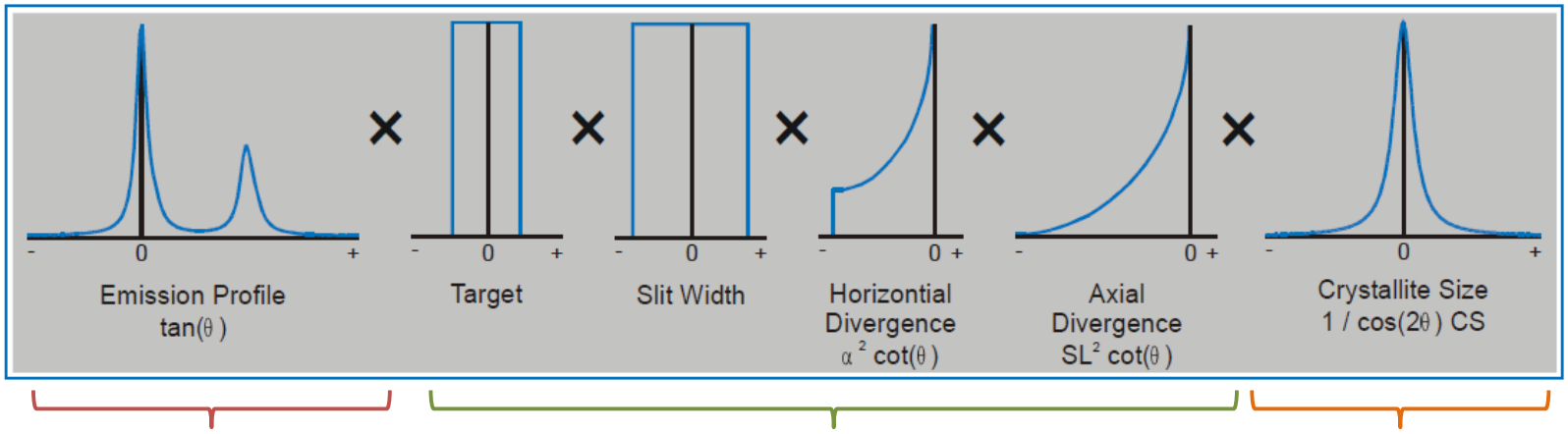
Why different peak shape?



Fundamental Parameters Approach FPA

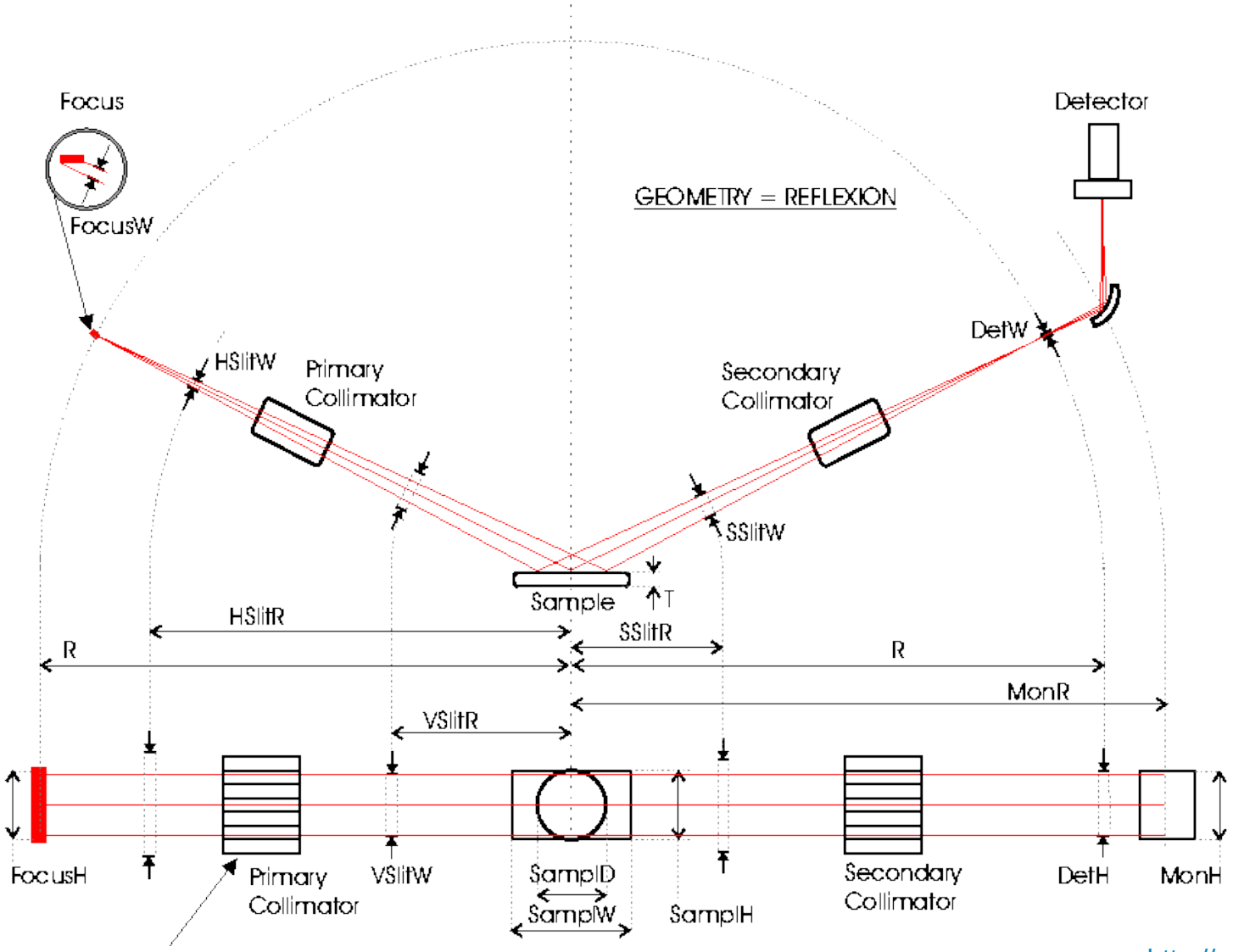
Observed peak shape = convolution of:

- Source emission profile (X-ray wavelength distribution from Tube)
- Every optical element in the beam path (position, size, etc.)
- Sample contributions (peak broadening due to crystallite size & strain)



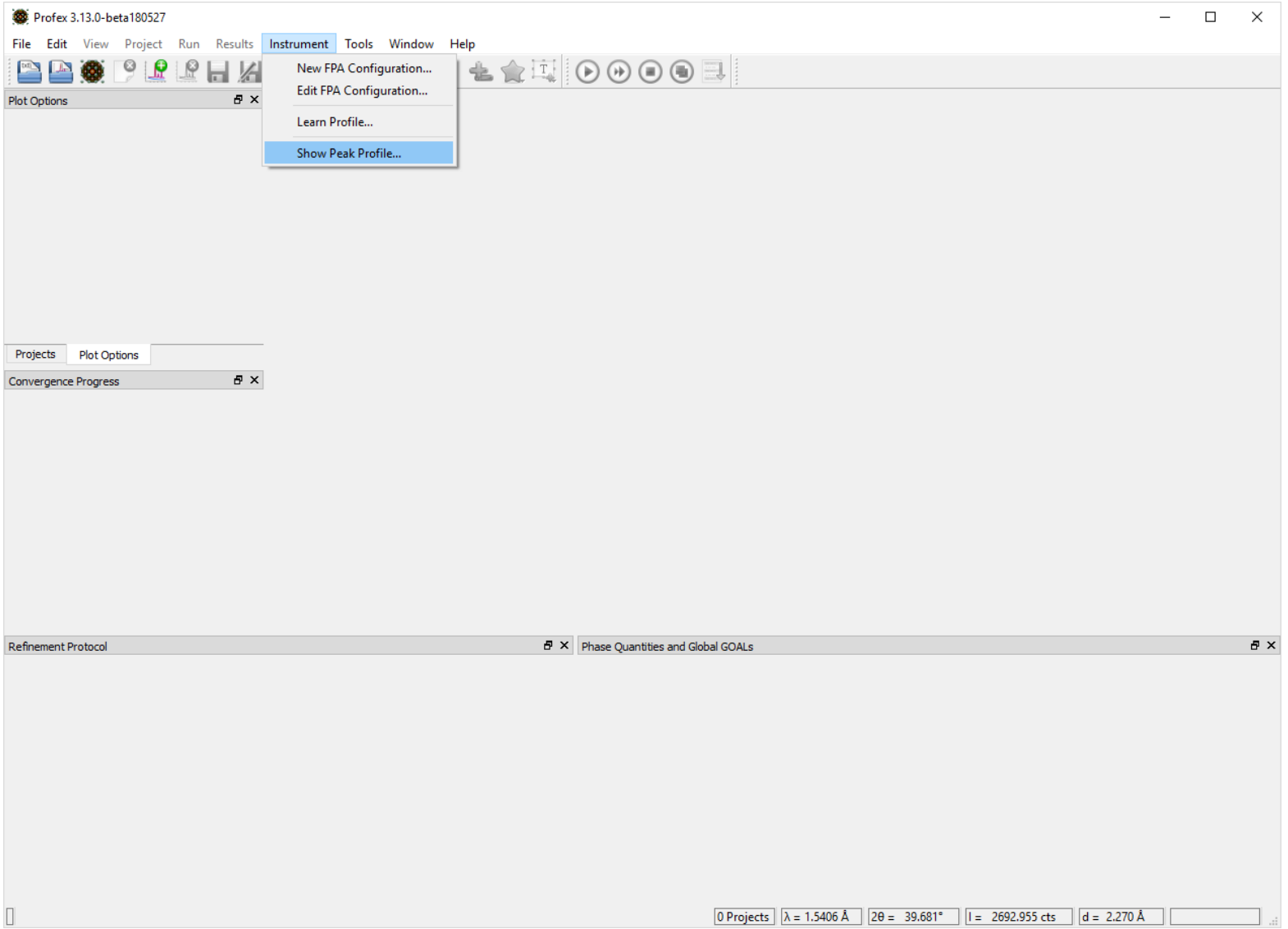
www.bruker.com

Fundamental Parameters Approach



http://www.bgmn.de

Visualize Peak Profiles



Visualize Peak Profiles